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ON THE CRYSTAL FORM OF METALLIC ZINC.

BY GEO. H. WILLIAMS AND WM. M. BURTON.

Of the crystal form of metallic zinc very little is definitely known. This element is generally regarded as hexagonal, and as probably isomorphous with the rhombohedral metals, arsenic, antimony, bismuth, and tellurium, but the basis of observation upon which such statements rest is extremely meagre. The production of remarkably perfect crystals of zinc, in the course of the determination, by one of the writers, of its atomic weight,[1] seems therefore of sufficient interest to warrant their study and description.

With the exception of certain casual and inaccurate statements by Berzelius, Berthier, and Laurent, the first account of zinc crystals was given by Nöggerath in 1836, who obtained them as the accidental product of a furnace near Lüttich. He describes them as hexagonal prisms, often barrel-shaped like corundum, and strongly striated parallel to the base.[2] G. Rose subsequently attempted to measure these crystals, but with only partial success. One crystal gave him in three consecutive zones, as the inclination of a pyramid to the basal pinacoid, the values 110° 35′–50′, 110° 31′–42′, 111° 45′–50′;[3] which are, so far as we can ascertain, the only measurements on zinc crystals which have heretofore been published. In 1848 Nicklès described crystals of zinc obtained by Favre while

[1] H. N. Morse and W. M. Burton: The atomic weight of zinc as determined by the composition of the oxide. This Journal **10**, 311.

[2] Krystallform des regulinischen Zinks. Ann. der Phys. Pogg. **39**, 223.

[3] Ann. der Phys. Pogg. **83**, 129, and Monatsber. Berl. Ak. Juli, 1850.

distilling the metal in an atmosphere of hydrogen, and considered them as pentagonal dodecahedrons,[1] but these forms Rose afterwards showed to be irregular polyhedral aggregates without symmetry.[2] Further observations have been made on the hexagonal form of zinc by Stolba, but these are unsupported by measurements.[3] In various alloys zinc is known to assume a regular form,[4] but in the pure state it is known only as hexagonal.

The absolute purity of the zinc obtained by successive distillations in a vacuum has been described by Morse and Burton (loc. cit.) Careful analysis disclosed no trace of any other substance, nor could any be discovered with Rowland's 20-foot concave grating spectroscope.

By the ordinary rapid distillation which took place in a horizontal glass tube placed in a combustion furnace, the zinc formed in globules on the top of the tube, and as these increased in size they dropped down, forming a solid bar of metal. The larger of the globules which remained on the upper portion of the tube when it was cooled became bounded by a multitude of bright plane surfaces; the smaller of these globules, when examined with a lens, were found to have formed minute barrel-shaped crystals terminated by a hexagonal basal plane, parallel to which their sides were finely striated.

Examination showed that neither of these varieties of crystals were suited for accurate measurement, and an attempt was therefore made by much slower distillation at a lower temperature to secure more perfect ones. Different parts of the tube were unequally heated, and kept for several hours at a temperature not far from the melting point of the metal. This attempt proved successful. Three different types of crystals were formed: spheroidal polyhedral aggregates, barrel-shaped crystals, and tabular hexagonal plates. Although the last named alone furnished crystallographic data, it will be of interest to describe each type.

Polyhedral Aggregates.—The larger globules which remain on the upper surface of the tube vary between one and eight millimeters in diameter, and become upon cooling what seem to be

[1] Sur la forme cristalline du zinc métallique. Ann. chim. phys. (3) **22**, 37, 1848.

[2] Ann. der Phys. Pogg. **85**, 293, 1852.

[3] J. prakt. Chem. **96**, 182, 1866.

[4] Rose: Ueber die Dimorphie des Zinks: Ann. der Phys. Pogg. **107**, 448, 1859. J. Cooke: Am. Jour. Science (2) **31**, 194, 1861; vid. also Rammelsberg: Handbuch d. krystallographisch-physikalischen Chemie **1**, 186. 1881.

at first glance brilliant but very complicated crystals. They are bounded by a multitude of planes, but a more careful examination shows that these are without symmetry of arrangement. Indeed, in no two is the arrangement the same. Fig. 1 shows an unusually simple form of this kind 4 mm. in diameter and 2½ mm. high, and Fig. 2 gives the projection of its faces on a plane surface. As a rule, however, these forms are more nearly spherical in shape, and bounded by a much greater number of planes. They are evidently what Nicklès mistook for pentagonal dodecahedrons, and in fact the planes frequently have a pentagonal shape. In reality they are, as G. Rose showed, complicated aggregates of crystals, similar to those formed by the cooling of a globule of pyromorphite after it has been fused before the blow-pipe. The fact of their aggregate structure is often well shown by the presence of finely striated surfaces, the striations running in many different directions, while in simple crystals they are always parallel to the basal plane. These aggregates are not entirely bounded by planes. Between these, curved surfaces of greater or less extent frequently occur, as shown in the figures.

Barrel-shaped Crystals.—The general character of these is shown in Fig. 3. They are always minute, never exceeding two millimeters in diameter. Their bases are sharply defined and hexagonal, but their sides are finely striated. It can also be seen under the microscope that these striations are not absolutely parallel, indicating that the little plates of which the crystal appears to be built up do not have their vertical axes in exactly the same line. On the reflecting goniometer these barrel-shaped crystals give a continuous "shimmer" reflex between planes inclined about 140° to the two basal pinacoids. There are indeed points in this continuous light band where the reflection is brighter than at others, but the examination of a number of crystals convinced us that they were unevenly distributed and unreliable. The brightest point, however, invariably occurred after a revolution of about 57° from the basal plane, indicating the position of the fundamental pyramid.

Tabular Crystals.—The third type of crystals, having a tabular habit, were produced only when the distillation of the zinc proceeded slowly and at a moderate temperature. These are more perfect and simpler in their crystal form, and are the only ones whose planes allowed of satisfactory measurement. Even these smallest and thinnest crystals are shown by the microscope to be

composed of piles of sharp hexagonal plates whose boundaries are parallel but not coincident. Rapid alteration in the size of these plates may produce very irregularly shaped crystals, as shown in Fig. 5. There is, however, an average decrease in their size as the pile grows upward, producing a gradation of the tabular into the barrel-shaped crystals. This method of superposition is represented in Fig. 6. The fact that the angles of these little hexagonal plates do not lie in the same line, although their sides are parallel, often produces a rough edge between the adjoining pyramidal faces. This projection of the hexagonal angles of the successive plates may form a pseudo-plane of the second order, as shown in Fig. 7. True planes of the second order also occur as truncations on one or more of the polar edges of the pyramids (see Figs. 3, 4, and 5), but these are very minute and more or less curved.

A series of measurements was made with the revolving stage of a microscope, for the purpose of detecting any possible variation in the plane angles of the hexagonal plates from 120°. The sharp boundaries allowed of very accurate adjustment, but no such disagreement could be discovered. The angles varied on either side of 120° only within the limit of the error of observation.

For purposes of exact measurement, small crystals of tabular habit (one millimeter or less in diameter) were alone found to be serviceable. Out of a large mass of these, only a few were found to be satisfactory, even when examined with a pocket lens; and of those thus selected, by no means all yielded results upon the goniometer. After carefully testing a number of crystals, seven were finally chosen as giving reflections which were sharp enough to be considered reliable. Each of these was measured in as many zones as possible, but it was only seldom the case that more than 90° could be measured from the base, as one-half the crystal was usually much less perfect than the other.

The strongest, though not in all cases the sharpest, reflection was obtained from a pyramidal plane whose inclination to the basal pinacoid was approximately 123°. This was, therefore, assumed as the unit pyramid. Three of the sharpest images were obtained at 122° 32′, 122° 33′ and 122° 33′; and as the angle 122° 33′ 24″ was obtained as the mean of all the measurements made upon the five crystals (yielding a total of eighteen zones) upon which this form was identified, this was taken as the basis for calculating the axial ratio, $a : c = 1 : 1.356425$.

The mean of five measurements of the polar angles of this same pyramid, made on three different crystals, gave 130° 20′, corresponding to the ratio $a:c = 1:1.3493$, but this may be regarded as less accurate than that first given.

The following is the table of angles measured on seven different crystals with a horizontal goniometer (Fuess's Model 2). The inclination is given in each case of the respective pyramidal plane to the basal pinacoid. When more than one zone was measured on a single crystal, the mean result is stated, and the number of zones upon which this average is based is given in parenthesis. The reflections of the signal were by no means all that could be desired, being sometimes broad, sometimes compound, and sometimes very faint. The sharpest image was given by the basal plane, and the next best by the fundamental pyramid. Very indefinite reflections were discarded, and it is believed that the results are as good as could be secured with the material at hand. In but few cases did the differences in similar angles reach a degree; for the most part they were far within this limit.

The required angles are calculated for the axial ratio, $a:c = 1:1.356425$.

Crystal.	$\frac{4}{3}$P.	$\frac{2}{3}$P.	P.
I.	138° 11′ (1)	...	...
II.	138 41 (2)	133° 24′ (3)	122° 32′ (3)
III.	...	134 00 (1)	122 34 (3)
IV.	...	...	122 47 (4)
V.	138 00 (1)	133 15 (1)	122 18 (4)
VI.	...	...	...
VII.	138 45 (2)	133 07 (3)	122 36 (4)
Mean,	138 24	133 27	122 33 24″
Calculated,	138 10	133 46	...
Difference,	+ 14′	— 19′	...

Crystal.	$\frac{4}{5}$P.	6P.	∞P.
I.	...	...	...
II.	...	95° 57′ (2)	89° 58′ (1)
III.	...	...	...
IV.	113° 18′ (1)	...	90 08 (1)
V.	...	96 42 (1)	90 08 (2)
VI.	112 34 (1)	96 15 (1)	...
VII.	114 05 (1)	96 10 (1)	90 04 (5)

	$\frac{6}{5}$P.	6P.	∞P.
Mean,	113° 19′	96° 18′	90° 05′
Calculated,	113 03	96 04	90 00
Difference,	+ 16′	+ 14′	+ 5′

No other angles were measured except the polar angles of the form P, which gave, as above stated, 130° 20′ as the mean of five determinations on three different crystals. An attempt was made to locate the pyramid of the second order, whose little plane on some of the crystals appeared quite brilliant. This was, however, unsuccessful. This face when best developed is curved and gives no reflex of the signal, while its minute size renders its accurate centering difficult. In one case (Crystal II), a reading of 117° 17′ was made as the inclination of this face to the basal plane, but it was accomplished without the signal, and cannot be regarded as satisfactory.

A large number of other pyramids of the first order undoubtedly exist, as is indicated by the almost continuous "shimmer" obtained from the barrel-shaped crystals, as well as by many faint reflections of the signal at points intermediate between the values given in the above table. In a single zone of Crystal II, the following series of readings lying between the forms $\frac{8}{5}$P and 6P was made from reflections of the signal, which, though faint, were fairly well defined: 104° 10′, 103° 19′, 100° 56′, 98° 42′.

These yield the symbols for four additional pyramids as follows:

	$\frac{8}{5}$P.	$\frac{7}{5}$P.	4P.	$\frac{12}{5}$P.
Observed,	104° 10′	103° 19′	100° 56′	98° 42′
Calculated,	104 20	103 28	101 04	98 23
Difference,	— 10′	— 9′	— 8′	+ 19′

Inasmuch, however, as it was possible to identify these pyramids only in one zone of a single crystal, they cannot be regarded as so characteristic as those planes found to occur in different zones of several crystals. No reflection corresponding to the angles given by Rose was observed on any of our crystals.

At first glance there is nothing about the distribution of the planes on the zinc crystals to indicate a rhombohedral character. Surely the unit pyramid (P) occurs with a holohedral development, as its presence was determined three times in four consecutive zones, and twice in three. Nor could any regularity be observed in the absence of the more obtuse pyramids $\frac{4}{7}$P and $\frac{8}{7}$P, for they were often present in two consecutive zones, while they

were wanting in others. The two acute pyramids $\frac{4}{3}$P and 6P were, however, in several instances observed to alternate with each other, as well in consecutive zones as on opposite sides of the prism in the same zone. This indicates a rhombohedral development of these forms, and as such they are represented on the ideal restoration of a tabular zinc crystal, Fig. 8.

Cohesion Phenomena.—As is well known, the cleavage of metallic zinc is very perfect parallel to the basal pinacoid. Brilliant cleavage surfaces could be readily obtained by splitting the little crystals with a knife-blade. No trace of any rhombohedral cleavage could be discovered. Rose observed that basal cleavage surfaces were frequently striated in three directions parallel to what he considered the faces of the rhombohedron. Similar striations were also observed intersecting at angles of 60°, but they were found to be pressure lines produced by cleaving the metal. Experiments were made with striking the point of a fine needle into the basal plane or cleavage surface, when a six-rayed star was produced, composed of systems of fine lines which were parallel to the boundaries of the crystal as well as to the pressure lines. The direction of these rays corresponds to those of the percussion figure (Schlagfigur) in mica, as shown in Fig. 9. Similar results were also obtained with bismuth and graphite. Attempts to produce secondary twinning lamellae by subjecting the zinc crystals to pressure were unavailing, as were also efforts to establish their symmetry by etching.

Relation to the Rhombohedral Metals.—Since the work of Rose, zinc has been regarded as rhombohedral, and as isomorphous with the elements arsenic, antimony, bismuth, and tellurium.[1] The axial ratio obtained from Rose's measurements, 2.177, does not, however, accord well with this assumption. The result obtained from our unit pyramid, on the other hand, agrees very closely with the ratios of these other metals.

Arsenic, 1 : 1.4025, Zepharovich (Sitzungsber. Wien. Ak. Vol. 71, 1875).

Antimony, 1 : 1.3236, Laspeyres (Zeitschr. deutsch. geol. Gesell. 1875).

Bismuth, 1 : 1.3035, Rose (Abh. Berl. Ak. 1849).

Tellurium, 1 : 1.3298, Rose (ibid.).

Zinc, 1 : 1.356425, Williams and Burton.

[1] Ueber die Krystallform der rhomboëdrischen Metalle, etc. Abhandlungen der Akad. der Wiss. in Berlin, 1849, p. 73.

The cleavage of zinc agrees with that of all except tellurium, but the habit of the crystals, in spite of the similarity in axial ratio, is altogether different. This may, however, also be said of the other members of this group.

The zinc crystals measured by us cannot be said to definitely show the rhombohedral character of the metal. Nevertheless, analogy indicates this; and on the supposition that the positive and negative rhombohedrons of the same symbol occur in equal development, there is nothing in the form of the hexagonal pyramids which is positively opposed to it.

Certain striking points of resemblance may be noticed between the crystallisation of zinc and the hexagonal and pseudo-hexagonal members of the chlorite group, chlorite, pennine, and ripidolite. Here, as in the case of all the approximately hexagonal minerals possessing a very perfect basal cleavage, like mica, graphite, or molybdanite, it is only under the most favorable possible conditions that the lateral planes are sufficiently well developed to allow of accurate determination. Moreover, the absence of those delicate optical tests which have done so much to establish slight variations from hexagonal symmetry in transparent minerals like mica, must ever leave the true nature of opaque crystals of the same habit in doubt.

Explanation of the Plates.

Plate I.

Fig. 1.—View from the side of a comparatively simple polyhedral aggregate of zinc, 2½x4 mm.

Fig. 2.—Projection of the same upon a plane passed through its center, showing curved surfaces between the planes.

Fig. 3.—Barrel-shaped crystal, 1½ mm. in diameter, with irregular edges between its pyramid planes, and indications of forms of the second order.

Fig. 4.—Thick tabular crystal, showing pyramid of the second order, generally curved.

Fig. 5.—Irregularly shaped crystal produced by the superposition of plates of unequal size.

Plate II.

Fig. 6.—Superposition of hexagonal plates of different size.

Fig. 7.—Diagram representing a tabular crystal composed of

1

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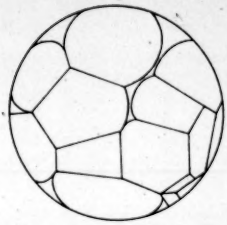

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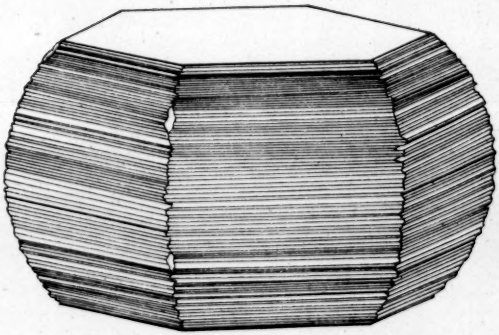

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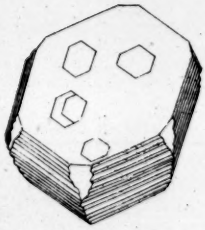

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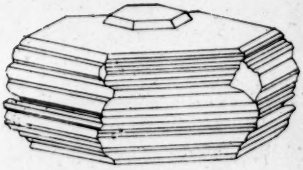

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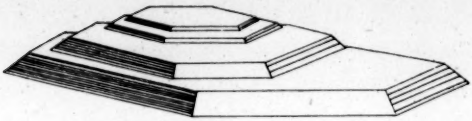

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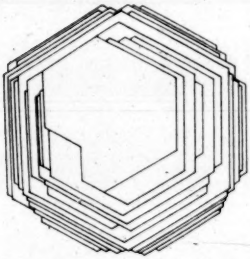

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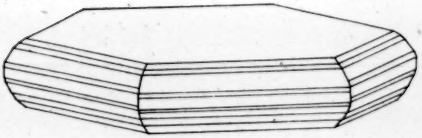

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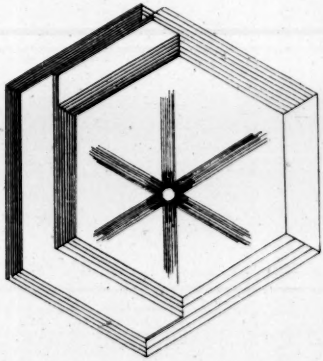

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superposed plates whose sides are parallel, but whose angles produce a pseudo-plane of the second order.

Fig. 8.—Ideal development of a tabular zinc crystal, showing the forms OP, $\frac{1}{4}$P, $\frac{3}{4}$P, P, $\frac{3}{2}$P (rhombohedral [?]), 6P (rhombohedral [?]), and ∞P.

Fig. 9.—Six-rayed star (percussion figure) produced by the point of a fine needle.

Contributions from the Laboratory of the United States Department of Agriculture.

XI.—BORACIC ACID AS A PLANT CONSTITUENT.

By C. A. Crampton.

In the year 1887 I examined 36 samples of wine, obtained in the local market, for adulterations. In applying a test for boracic acid to these samples, I was surprised to find that all but two gave a distinct test for this element. It did not seem possible that it could have been added to the wines for purposes of preservation, for it could hardly have obtained so extensive a use for this purpose; and, besides, in many cases I found other preservatives present, salicylic acid and sulphurous acid, which are much more efficient for this purpose than borax. Yet I did not feel justified in concluding that it was a normal constituent of the wine, for my samples were not such as could be properly used as the basis of such an assumption. In fact, I was at a loss to account for the matter, and passed it over in the Bulletin referred to,[1] expecting to give it further attention at a later period. Baumert[2] had already published an article giving the results of a very thorough examination made by him upon some California wines. He had the same experience I did in making his tests for boracic acid, finding it in every sample he examined. He was loth to believe that it could have found so extensive a use as a preservative, and ventured the hypothesis that it had been taken up by the plant from the soil, knowing that some California soils contain borax. But his samples were only 8 in number, and all came from California. My samples came from various parts of the United

[1] Bulletin No. **13**, Part III, U. S. Department of Agriculture, Chemical Division, p. 363.
[2] Landw. Vers. Stat. **33**, 39.

States, including California, and I obtained the test in wines from places as widely distant from one another as New York, Ohio, North Carolina, and Virginia. So the acceptance of the hypothesis that it was derived from the soil would necessarily imply that the soils of all these localities contained boracic acid as one of their constituents, and I hesitated about deciding that such was the case from the small amount of evidence at hand. In the meantime, Professor Rising, of California, stimulated to the defense of the purity of the natural wines of his State from the implication cast upon them by Baumert's and my analyses, set himself to the task of proving that boracic acid was a normal constituent of natural grape juice. The following extract from a letter he sent to me in July, 1888,[1] shows the results of his work. He says:

"We have proved beyond any question, I think, the presence of boracic acid in many unadulterated California wines. In addition to the test with turmeric paper, we have obtained the flame test so decided that there can be no doubt. I have just received a new spectroscope, and I shall hope by its aid to settle this point beyond all question. Our method of work is as follows: 50 to 100 cubic centimeters of wine are evaporated in a platinum dish, ignited and burned to ash. Part of this ash is transferred to a platinum spoon; such an one as is used for blow-pipe work answers very well. A few drops of the strongest H_2SO_4 (I have used a 96–98 per cent. acid), then alcohol, is added, and then lighted and immediately blown out, and relighted and again extinguished. The first flash will show the acid very distinctly if it is present."

Thus the fact may be said to be established that boracic acid is a normal constituent of *California* grapes. But others have made investigations on this point, and abundant evidence has been obtained to the effect that it is to be found in wines in many different parts of the world. Baumert gives, in a recent number of the *Berichte*,[2] the results obtained by himself and others in this direction. Soltsien[3] concluded, from the observations of himself and others, that boracic acid was not an unusual constituent of wine ash. Ripper[4] found it as a normal constituent not only of 1000 different samples, including both German and foreign wines, but

[1] Published in full in Bulletin No. 19, Chem. Div. U. S. Dept. Agriculture, p. 38.
[2] 21, 3290.
[3] Pharmaceutische Zeitung 33, 312.
[4] Weinbau und Weinhandel; Organ des Deutschen Weinbau Vereins, No. 36, 1888.

also of various parts of different grape stocks. He also succeeded in isolating it as fluoborate of potassium from 2 liters of a Riesling wine. Baumert himself says he has made it a practice for the last three years to test every wine that came into his hands for boracic acid, and found it present in every case without exception! These samples included German, Spanish and French wines, also wines from grapes grown in Saxony, Thuringia, and musts from Freyburg and Naumburg. He also tested for it in all parts of grape-vines grown near Halle—in the leaves, wood, fruit, stems, etc.—without failing to obtain positive results in any case. Soltsien[1] obtained like results on the so-called wild grape-vine (*Ampelopsis quinquefolia*).

There can no longer be any question, therefore, in view of this mass of evidence, that boracic acid is a normal and frequently occurring constituent of the grape plant; and that this is true not only as regards wines grown in any particular section, but holds good of a considerable part of Europe and of the United States. The peculiar part of my own analyses now seems to be that I found any samples which did *not* give the test. (There were two wines among those I examined in which I could get no test for boracic acid; both were Catawba wines; one was made in Pleasant Valley, N. Y., the other in Bass Island, a small island in Lake Erie, northeast of Toledo.)

If boracic acid is so universal a constituent of the grape plant, why not of other plants as well? This occurred to me as soon as I saw the articles containing the results of the work of the European chemists upon the grape-vine, and I immediately proceeded to apply the test to all the samples of plant-ash we had on hand in the laboratory. Mr. A. E. Knorr, of this department, has been engaged lately in the prosecution of the chemical part of an inquiry into the disease known as the "yellows" in peach trees. In the course of his work he had occasion to make analyses of the ash of various parts of the peach trees, portions of which he still had on hand. At my suggestion he applied the turmeric paper test to all these samples, and the result was to show the presence of boracic acid in each and every case. The samples included ash from the following parts of the plant: leaves, stems, wood, and fruit, including kernels. I then applied the test to all the plant ashes I could find in the laboratory, with the following results:

[1] Phar. Zeit. **33**, No. 90.

Thirteen different samples of ash from various parts of the fruit of the watermelon vine gave good tests in every case. These included every part of the fruit: rind, pulp, juice and seed, and were obtained from watermelons purchased in Washington, D. C.

A sample of ash from apples gave no test.

A sample of ash from sugar-beets grown in Oregon gave no test.

A sample of ash from southern sugar-cane grown in Louisiana gave no test.

In connection with the results of the test on ash from apples, I would say that all the samples of cider (12) included in my investigation, published in Part III, Bulletin No. 13, were subjected to the test for borax, with negative results in each case.

From the results of these few tests it is evident that the occurrence of boracic acid as a constituent of plants is much more general than has been supposed. If it is found so constantly in grape juice in different parts of the world, and in such dissimilar plants as the peach tree and the watermelon vine, I have no doubt but that it will be found in a great many other plants, now that the attention of chemists has been called to the matter. No analysis of plant-ash will be complete in the future without a search for this constituent. I hope to be able soon to make a quantitative estimation of it in some of the samples I have on hand.

Considering the fact of the relatively small number of mineral substances found in plants, and the importance which has been accorded them in chemical science, it seems strange that the occurrence of this element has remained so long unknown. In the brief search I have been able to make in chemical literature I can find no mention of its being found as a constituent of plants. It must be derived from the soil, of course, but none of the authorities I have consulted speak of its occurrence outside of the localities where it is in sufficient quantities to constitute a mineral deposit and a commercial source of supply. Hilgard[1] speaks of its occurring in the so-called alkali soils of California, but these might be included in the above category, as it is from similar sources that all our supply of borax in this country is drawn.

Baumert[2] could obtain no test in a specimen of soil taken from a wine-growing district in California. Doubtless the test would be more difficult to obtain from a soil than from the ash of the plant

[1] 10th U. S. Census Report. [2] Landw. Ver. Stat. **33**, 87.

grown upon it, as the salt would be accumulated in the latter.[1] Spectroscopic examination would probably prove useful in the case of soils. In my experience, the test for boracic acid by means of the peculiar red color imparted to turmeric paper is fully as delicate as the flame test and much more satisfactory. I obtained the former in many cases where I could not get the latter satisfactorily, and I have found difficulty in getting the greenish flame where I made tests upon known but small quantities of borax. The turmeric test is not only delicate but very distinctive, the only salt giving a coloration which could possibly be mistaken for it being ferric chloride, and the brownish color produced by this does not very closely resemble the characteristic reddish color produced by boracic acid, and, moreover, does not undergo the change to greenish black on dipping into an alkali solution which is developed in the latter. Baumert[2] relies upon this test, and considers the precautions superfluous which Ripper and Soltsien observed in its application.

The instances where I failed to obtain a test in some of the ashes examined show either that this element is not universally distributed in all soils, or that some plants have a selective affinity for it, absorbing it from all soils while other plants reject it. The latter would seem to be the more probable hypothesis from the evidence we have at present, but further investigations will be necessary to establish this point.[3] It is a most interesting subject, and I hope we will soon have further light thrown upon it. Aside from the interest which attaches to its occurrence *per se*, its relation to the examination of food materials for artificial preservatives which have been fraudulently added, makes it a matter of direct practical importance. Boracic acid shares with salicylic acid, sulphites, hydronaphthol,

[1] It is interesting to note in this connection the surprisingly large percentage of boron found by Messrs. Gooch and Whitfield in mineral waters from the Yellowstone Park (Bull. No. 47, U. S. Geological Survey). They found it present in nearly all of the samples examined, and in some cases to the extent of nearly 3 per cent. of the total solid matter. These waters are of course peculiar in their origin, but perhaps a search for this element in water analysis in general would develop a more extensive distribution of it than has been heretofore supposed. I doubt if a test for it is often included in an ordinary water analysis.

[2] Op. cit. p. 3291.

[3] Prof. F. W. Clarke, of the U. S. Geological Survey, has suggested to me that perhaps a study of the origin of the soil upon which boron-bearing plants grew would have some bearing upon the subject of the distribution of this element. His idea was that soils of granitic origin would be likely to contain it, while those derived from the disintegration of limestone formations might not, and he called my attention to the fact that both the wines in which I was unable to prove its presence were from limestone districts. Prof. Clarke also reminded me of the volatilisation of boracic acid when an alcoholic solution of it is evaporated, and suggested the precaution, which I would recommend to chemists, of fixing the acid by the addition of an alkali when making the test in wines, so that no trace would be allowed to escape.

etc., the distinction of being used for such purposes, and until we have more definite information as to the extent and limits of its existence as a normal constituent of vegetable matter, we cannot rely, as heretofore, upon a mere qualitative proof of its presence in a food material, such as wine, canned goods, etc., as an indication of fraud in the preparation of the material examined.

XII.—SPECIFIC GRAVITY OF SOME FATS AND OILS.

By C. A. Crampton.

During the investigation of fats and oils made in this laboratory the past year, the results of which will shortly be issued as Part IV, Bull. No. **13,** Chemical Division, I had occasion to determine the specific gravity of the large series of samples examined. This was done by means of the Archimedian method, as recommended by Allen,[1] using the plummet of a Westphal balance, but making the weighings with an ordinary balance. The plummet was ground to displace 5 grams of pure water at a temperature of + 35° C. The method gave very good results, and was easy and rapid in its execution—a very desirable condition, in view of the large number of samples. Some of the fats, however, were solid at 35°, and their densities could not be determined in this way, except by maintaining quite a high degree of heat near the balance, which was not attempted. These were taken with an ordinary specific gravity flask with a perforated stopper, which was filled with the melted fat at convenient temperatures, then allowed to cool, and weighed. In this way I took the specific gravities of the more important samples used in the investigations, not only the harder fats, such as stearines, but also the lards and oils. Being interested in examining for myself the correctness of the figures given by Allen for the expansions of these bodies, I determined the specific gravities upon all the samples at high temperatures, and from these data the coefficients of expansion in each case. As these samples were typical in many cases, and as all were subjected to a very thorough and careful examination in respect of their other properties (the results of which will be set forth in the Bulletin), I append a table containing the results obtained, as they may prove valuable in establishing standards for

[1] Organic Analysis 2, 14, foot-note.

this important class of food materials, the composition of which is attracting much attention at present among chemists.

All the determinations were made very carefully, and the figures given are in all cases the average of two or more duplicates. In the densities taken at low temperatures, the flasks filled with the sample were placed in a vessel containing water somewhat above the temperature at which the determination was to be made, and when it had dropped to this point they were carefully stoppered, taken out of the vessel, allowed to cool, and weighed. The determinations at high temperatures were made by placing the flasks in an oil-bath. The heat was raised to as high a point as was deemed safe, and at the temperatures used, 190°–200° C., there was scarcely a darkening of the contents of the flasks, and I am convinced that no decomposition had taken place which would alter appreciably the density of the sample. From the densities taken at these two widely different temperatures, the mean increase in density and the mean coefficient of expansion were determined for each sample. The formula used for this was the one usually given in the books,[1] $\delta = \frac{D'_o - D_o}{(t' - t)D_o}$, in which

D_o = density at the lower observed temperature;
D'_o = " " higher " "
t = lower temperature;
t' = higher "

although it appears to me that the formula $\frac{D_o - D'_o}{(t' - t)D_o}$ would be more correct, or $\frac{D_o - D'_o}{(t' - t)\left(\frac{D_o + D'_o}{2}\right)}$ still better. Great confusion exists in chemical literature in the expression of specific gravities. I have referred all my results to water at + 4° C., believing that eventually all specific gravities will be stated in these terms, as is the custom in continental Europe. The absolute densities are calculated from the formula $\Delta = \delta + \kappa$, in which

Δ = coefficient of absolute expansion in glass;
δ = " " apparent " "
κ = " " cubical expansion of glass = .000025.

The weights were not reduced to a vacuum, and no correction was made for the thread of mercury projecting above the bulb.

[1] Watts' Dictionary **3**, 71.

Specific Gravities of Fats and Oils at Various Temperatures, with Mean Coefficients of Expansion.

DESCRIPTION.	Temperature.	Apparent Specific Gravity in Glass Vessels.	Absolute Specific Gravity.	Temperature.	Apparent Specific Gravity in Glass Vessels.	Absolute Specific Gravity.	Range in Temperature.	Mean Difference in Specific Gravity for each Degree Centigrade Apparent in Glass Vessels.	Mean Coefficient of Expansion Apparent in Glass Vessels.	Mean Coefficient of Expansion, Absolute.	Calculated. Specific Gravity $d = +15^{\circ}$ C. Apparent.	Calculated. Specific Gravity $d = +40^{\circ}$ C. Apparent.	Calculated. Specific Gravity $d = +90^{\circ}$ C. Apparent.	Calculated. Specific Gravity $d = +100^{\circ}$ C. Apparent.
Lards.														
1. Leaf Lard rendered in Laboratory U. S. Dept. Agriculture	+40° C.	.89679	.89769	+190° C.	.80475	.80940	+40° to +190° C	.0006136	.0007624	.0007649	.91181	.89679	.89065	.88997
2. Intestinal Lard rendered in Laboratory U. S. Dept. Agriculture	+4° "	.89635	.89725	+4° "	.80315	.80780	" "	.0006213	.0007736	.0007761	.91157	.89635	.89014	.88907
3. Head Lard rendered in Laboratory U. S. Dept. Agriculture	"	.89816	.89906	"	.80512	.80977	" "	.0006203	.0007704	.0007729	.91336	.89816	.89195	.88994
				+95°										
4. Squire's Pure Lard, made by J. P. Squire & Co., Boston, Mass	"	.89700	.89790	+4°	.86319	.86546	+40° to +95°	.0006147	.0007122	.0007147	.91206	.89700	.89085	.86012
				+187°										
5. Cassard's Pure Lard, made by Cassard & Co., Baltimore, Md	"	.89848	.89938	+4°	.80888	.81345	+40° to +187°	.0006095	.0007535	.0007560	.91341	.89238	.89848	.86191
				+190°										
6. [1]Armour's "Compound Lard," made by Armour & Co., Chicago, Ill	"	.89940	.90030	+4°	.80646	.81111	+40° to +190°	.0006196	.0007683	.0007708	.91458	.89940	.89320	.86222
7. Armour's "Compound Lard," made by Armour & Co., Chicago, Ill	"	.89854	.89944	"	.80522	.80987	" "	.0006221	.0007726	.0007751	.91378	.89232	.89854	.86121
8. Fairbanks' "Compound Lard," made by Fairbanks & Co., Chicago, Ill.	"	.90000	.90090	"	.80724	.81189	" "	.0006184	.0007660	.0007685	.91515	.90000	.89382	.86289
Lard Stearines.														
	+50°			+200°										
1. Lard Stearine used in compounding Armour's Compound Lard	+4°	.88836	.88951	+4°	.79579	.80069	+50° to +200°	.0006171	.0007755	.0007780	.90965	.89453	.88836	.85750
2. Lard Stearine used in compounding Fairbanks' Compound Lard	"	.88850	.88965	"	.79677	.80167	" "	.0006115	.0007675	.0007700	.90959	.89461	.88850	.85792
Beef Fat and Oleostearines.														
	+50°			+190°										
1. Pure Beef Fat from the testicle, obtained from Prof. S. P. Sharpless	+4°	.88998	.89113	+4°	.80289	.80754	+50° to +190°	.0006221	.0007748	.0007773	.91144	.89620	.88998	.85888
				+200°										
2. Oleostearine used in compounding Armour's Compound Lard	"	.88615	.88730	+4°	.79487	.79977	+50° to +200°	.0006084	.0007656	.0007681	.90714	.89223	.88615	.85572
3. Oleostearine used in compounding Fairbanks' Compound Lard	"	.88523	.88638	"	.79286	.79776	" "	.0006158	.0007767	.0007792	.90647	.89138	.88523	.85444
	+40°			+190°										
Cottonseed Stearine obtained from Prof. D. Wesson	+4°	.90313	.90403	+4°	.80689	.81154	+40° to +190°	.0006416	.0007951	.0007976	.91884	.90313	.89671	.86463
Cottonseed Oils.														
	+23°			+190°										
1. Crude Cottonseed Oil obtained from Prof. D. Wesson	+4°	.91548	.91595	+4°	.81118	.81583	+23° to +190°	.0006245	.0007699	.0007724	.92016	.90486	.89862	.86739
2. Crude Cottonseed Oil obtained from Southern Cotton Oil Trust	"	.91744	.91791	"	.81573	.82038	" "	.0006090	.0007466	.0007491	.92200	.90708	.90099	.87054
3. [2]"Summer Yellow" Oil obtained from Southern Cotton Oil Trust	"	.91589	.91636	"	.81021	.81486	" "	.0006328	.0007813	.0007838	.92063	.90514	.89880	.86716
4. "Summer White" Oil obtained from Southern Cotton Oil Trust	"	.91578	.91625	"	.80959	.81424	" "	.0006359	.0007858	.0007883	.92055	.90497	.89861	.86681
	+24°													
5. "Winter Yellow" Oil obtained from Southern Cotton Oil Trust	+4°	.91623	.91673	"	.80525	.80990	+24° to +190°	.0006685	.0008302	.0008327	.92191	.90553	.89885	.86542
6. "Winter White" Oil obtained from Southern Cotton Oil Trust	"	.91636	.91686	"	.81017	.81482	" "	.0006397	.0007896	.0007921	.92179	.90612	.89972	.86774
	+23°													
7. Refined Cottonseed Oil used in compounding Armour's Compound Lard	+4°	.91667	.91714	"	.80925	.81390	+23° to +190°	.0006432	.0007948	.0007973	.92150	.90573	.89930	.86714
Olive Oils.														
	+23°			+190°										
1. Pure Olive Oil obtained from Z. D. Gilman, Washington, D. C	+4°	.91079	.91126	+4°	.80430	.80885	+23° to +190°	.0006377	.0007928	.0007953	.91557	.89995	.89351	.86168
2. Pure Olive Oil obtained from Prof. S. P. Sharpless	"	.91034	.91081	"	.80538	.81003	" "	.0006285	.0007804	.0007829	.91505	.89965	.89337	.86194

[1] Armour's Compound Lards are made by the following formulæ, according to affidavits filed with the samples:

	Regular (No. 7 of above table).	"Export" (No. 6 of table).
Lard	67 per cent.	59 per cent.
Oleostearine	15 "	18 "
Refined Cottonseed Oil	18 "	23 "
	100	100

[2] Trade terms used to designate different grades of refined oils.

The specific gravities of the different samples at various temperatures are also given in the last columns of the table, these having been calculated by means of the coefficients of expansion.

It will be seen that the results confirm, in the main, Allen's[1] conclusions in regard to the generally uniform rate of expansion of all fats and oils. The average increase in density in my samples would be rather lower than the figure he gives (.00064) for each degree C., as his figure was calculated from the formula $\delta = \frac{D_o - D_o'}{(t'-t)D_o}$. Kopp[2] gives a figure slightly higher than mine for the mean absolute expansion-coefficient of olive oil, viz. .00080348.

In the lards and oils in the above table I also determined the density by the plummet at + 35° C. These results, together with the results calculated from the flask determinations, so as to make the figures comparable, are given in the following table:

Comparison of Results with Plummet and with Specific Gravity Flask.

	With Plummet. $d = \frac{+35^\circ \text{ C.}}{+35^\circ}$	With Specific Gravity Flask. $d = \frac{+35^\circ \text{ C.}}{+35^\circ}$
Lards.		
1	.9058	.90508
2	.9047	.90484
3	.9066	.90652
4	.9044	.90523
5	.9067	.90671
6	.9069	.90797
7	.9068	.90667
8	.9080	.90816
Cotton Seed Oils.		
1	.9151	.91391
2	.9164	.91510
3	.9134	.91377
4	.9132	.91357
5	.9154	.91412
6	.9138	.91475
7	.9133	.91452
Olive Oils.		
1	.9076	.90848
2	.9080	.90811
Mean,	.9098	.90985

[1] Op. cit. p. 20.

[2] Ann. Chem. (Liebig) **93**, 129.

This short series of comparisons adds testimony to the accuracy of the Archimedian method for taking specific gravities. It is certainly a most rapid and convenient method for fats and oils. I went through nearly the entire series of samples used in our lard investigation, about 150 in all, in three days. I would call attention to a slight inaccuracy in Allen's description of the method. On page 14 (Vol. II), he says, "The plummet should have a displacement of exactly 5 *cubic centimeters*" (in water). This should, of course, be 5 *grams*, otherwise he would be comparing *volume* with *weight*, as it is the *weight* of the sample displaced which is used as the numerator of the fraction of which the *weight* of water displaced is the denominator in the expression of its specific gravity. The error would not be so great where the volume and density of water were taken as being identical at 15.5° C., but still quite an appreciable error would be introduced when the determination on the sample was made at 35°–50° C., as on a fat for example. There is much need for more exact mathematics in calculating specific gravities, and more uniformity in methods of expressing them among chemists is greatly to be desired.

Contributions from the Sheffield Laboratory of Yale University.

XXXI.—ON NITRO-DERIVATIVES OF OXALTOLUIDE.

By W. G. Mixter and F. Kleeberg.

Ortho-oxaltoluide.—Ladenburg,[1] by heating equal parts of *o*-toluidine and anhydrous oxalic acid, obtained polyformtoluide, melting point 211°. When, however, *o*-toluidine is heated with half its weight of crystallised oxalic acid to 190°, *o*-oxaltoluide is formed, and apparently no polyformtoluide. That is, with an excess of oxalic acid polyformtoluide results, and with an excess of toluidine oxaltoluide. We heated a mixture of oxalic acid and *o*-toluidine cautiously in a flask so that but little toluidine escaped with the vapor of water, and when the temperature of the molten mass had risen to 190°, it was poured into dilute hydrochloric acid. The lumps were broken up and the product was thoroughly washed with water. It was further purified by solution in boiling

[1] Ber. d. chem. Ges. **10**, 1128.

alcohol, from which it crystallised on cooling. An analysis of the preparation gave results which corresponded closely with the composition of oxaltoluide; but since this compound differs empirically from formtoluide by one atom of hydrogen, the analysis does not prove its purity. Moreover, our preparation melted at 199°–201°, or above the melting point, 189°, given by Mauthner and Suider[1] for *o*-oxaltoluide, which was first obtained by them by heating together ethyl oxalate and *o*-toluidine. The ready solution of our preparation of *o*-oxaltoluide in hot alcohol indicated that it was, at least, not largely mixed with polyformtoluide, which is only slightly soluble in the same solvent. Further, we prepared *o*-oxaltoluide as described by Mauthner and Suider, and found it to have the same melting point as that from heating oxalic acid and toluidine, and also found the preparations by the two methods to have identical properties. The yield of *o*-oxaltoluide is considerably larger with oxalic acid than when ethyl oxalate is used.

Tetra-nitro-o-oxaltoluide. — *o*-Oxaltoluide, 19.7 grams, was added slowly to 210 cc. of fuming nitric acid, and the clear red solution obtained was heated on a water-bath to boiling and then poured into cold water. The yellow product which separated was washed thoroughly with water and dried at 100°. The yield was 25 grams. The following analyses were made by Mr. F. O. Walther, who commenced the investigation in this laboratory, but did not have time to complete the work before leaving:

I. 0.5243 gram gave 82.87 cc. N at 16.7° and 769.1 mm. 0.4091 gram gave 0.1058 gram H_2O and 0.6415 gram CO_2.

II. 0.2596 gram gave 41.62 cc. N at 16.5° and 764.4 mm. 0.3981 gram gave 0.1098 gram H_2O and 0.6266 gram CO_2.

	Theory.	I.	II.
C_{16}	42.86	42.76	42.92
H_{12}	2.68	2.87	3.08
N_6	18.75	18.93	19.10
O_{10}	35.71	...	...

In order to determine the constitution of this tetranitro-oxaltoluide, the following experiments were made: First, 12 grams of it were digested with a boiling solution of potassium hydroxide (density 1.27) until ammonia ceased to come off. On adding hydrochloric acid, carbon dioxide was copiously evolved, and a

[1] Monatsh. der Chemie 7, 233.

black substance separated which was washed, dissolved in ether, filtered, and the solution evaporated. The tarry residue remaining appeared to be a mixture. Another portion of tetranitro-oxaltoluide was digested with a very dilute solution of potassium hydroxide, in which it dissolved completely. Hydrochloric acid was then added to the solution, and the yellow precipitate obtained was analysed and found to be tetranitro-oxaltoluide. Next, tetranitro-oxaltoluide was dissolved in concentrated sulphuric acid, the temperature of the mixture being gradually raised to 150°. The solution, after cooling, was poured into water, and the yellow precipitate which formed was washed, and, after recrystallising from hot alcohol, melted at 208°, the melting point of dinitro-*o*-toluidine, $C_6H_3\overset{1}{C}H_3\overset{2}{N}H_2\overset{3}{N}O_2\overset{5}{N}O_2$, described by Staedel.[1] In order to prove conclusively the constitution of the dinitro-toluidine in hand, it was converted into dinitro-toluene, as follows: It was added to concentrated nitric acid, and nitrous fumes passed through the mixture, which was kept cool, and was finally poured into boiling absolute alcohol. The product, after recrystallising, melted at 90°, thus proving its identity with the symmetrical dinitro-toluene described by Staedel, having the constitution $C_6H_3\overset{1}{C}H_3\overset{3}{N}O_2\overset{5}{N}O_2$. From these results it follows that tetranitro-*o*-oxaltoluide has the constitution

$$\begin{array}{l} \overset{1}{C}OCH_3\overset{2}{N}HC_6H_2\overset{3}{N}O_2\overset{5}{N}O_2 \\ | \\ COCH_3NHC_6H_2NO_2NO_2. \\ \quad 1 \quad 2 \qquad\quad 3 \quad 5 \end{array}$$

It is white, slightly soluble in hot absolute alcohol and glacial acetic acid, insoluble in ether and benzene, but dissolves readily in warm nitrobenzene, from which it crystallises on addition of absolute alcohol. It decomposes without showing a sharp melting point at about 270°.

An attempt was made to obtain a hexnitro-derivative by adding 10 grams of *o*-oxaltoluide to 100 cc. of red fuming nitric acid, and after complete solution adding 100 cc. of concentrated sulphuric acid. The whole was heated over a lamp to boiling, then allowed to cool and poured into snow. The product after drying weighed 11.5 grams. Two determinations gave 19.43 and 19.32 per cent.; calculated for hexnitro-oxaltoluide 20.82 per cent. These results indicate an impure tetranitro-oxaltoluide.

[1] Ber. d. chem. Ges. **14**, 900.

The *p*-oxaltoluide used in the following experiments was made according to the method described by Hübner,[1] by heating together equal parts of *p*-toluidine and oxalic acid. The product was treated with boiling water and finally with boiling alcohol.

Dinitro-p-oxaltoluide.—This compound was obtained by Hübner[2] by adding *p*-toluidine to red fuming nitric acid. We have prepared the same substance by using 15 parts of nitric acid of density 1.4 and boiling for five minutes.

Tetranitro-p-oxaltoluide.—This compound is formed when *p*-oxaltoluide is nitrated by hot red fuming nitric acid, or by a mixture of this acid and concentrated sulphuric acid, as shown by the following results: *p*-oxaltoluide, 5 grams, was added gradually to 50 cc. of fuming nitric acid, in which it dissolved completely. The solution on heating on a water-bath for a few minutes deposited crystals. The mixture was then poured into cold water, when a further separation occurred. The product after washing and drying at 100° weighed 5.7 grams. It is designated as A.

Another portion of 5 grams of *p*-oxaltoluide was added to a mixture of 50 cc. of fuming nitric acid and 50 cc. of sulphuric acid. The reaction was very violent and the yield was 5 grams. This product is designated as B.

A third portion of 5 grams of *p*-oxaltoluide was added to 100 cc. of fuming nitric acid, and then 100 cc. of concentrated sulphuric acid were poured in. Yellow crystals separated on shaking. The mixture was heated on a water-bath for ten minutes, then poured into cold water, filtered, washed free from acid, and dried at 100°. The product, designated as C, weighed 4.7 grams.

Analysis of A.—0.3106 gram gave 0.4817 gram CO_2 and 0.0762 gram H_2O. 0.457 gram gave 71.17 cc. N at 7.3° and 755 mm.

Analysis of B.—0.4520 gram gave 69.6 cc. N at 7.2° and 760.2 mm.

Analysis of C.—0.3738 gram gave 0.5801 gram CO_2 and 0.0935 gram H_2O. 0.4187 gram gave 63.82 cc. N at 5.6° and 767.4 mm.

	Theory.	A.	B.	C.
C_{16}	42.86	42.29	...	42.32
H_{12}	2.68	2.72	...	2.77
N_6	18.75	18.93	18.85	18.94
O_{10}	35.71	...	...	...
	100.			

[1] Ann. Chem. (Liebig) **209**, 371.

[2] Ber. d. chem. Ges. **8**, 474.

The tetranitro-*p*-oxaltoluide yielded, when saponified by a hot dilute solution of potassium hydroxide, a dinitrotoluidine melting at 168° and easily soluble in alcohol, corresponding to the one described by Beilstein[1] with the constitution $C_6H_2\overset{1}{C}H_3\overset{2}{N}O_2\overset{4}{N}H_2\overset{6}{N}O_2$. The tetranitro-*p*-oxaltoluide has therefore the constitution

$$\begin{array}{l} CO\overset{4}{N}HC_6H_2\overset{1}{C}H_3\overset{2}{N}O_2\overset{6}{N}O_2 \\ | \\ CO\underset{4}{N}HC_6H_2\underset{1}{C}H_3\underset{2}{N}O_2\underset{6}{N}O_2. \end{array}$$

It is insoluble in the ordinary solvents, but readily soluble in warm nitrobenzene. Both it and the corresponding ortho-compound do not yield with potassium hydroxide a dinitrotolyloxamide. In conclusion it may be stated that the tetranitro-derivatives of ortho- and para-oxaltoluide are easily made, and hence are good compounds from which to prepare dinitrotoluidines. We have not obtained satisfactory results in attempting to nitrate oxalxylidine.

A METHOD FOR THE DETECTION OF CHLORINE, BROMINE, IODINE, AND SULPHUR IN ORGANIC COMPOUNDS.

By Charles W. Marsh.

In testing for sulphur according to Schönn[2] by heating an organic substance with metallic sodium in a closed tube, dissolving the sodium sulphide formed in water, and adding a solution of sodium nitro-prusside, the inconvenience of working with sodium, and the precautions necessary in heating the sodium and substance, and in adding water to the contents of the tube, led the writer to look for another metal to replace the sodium. This metal when heated with organic bodies should decompose them and combine with the halogens and sulphur, or, if the substance were decomposed by heat, would enter into like combination.

Magnesium in fine powder has also been recommended by Schönn,[3] but only for the estimation of sulphur. He heats the substance with powdered magnesium in a hard glass tube, allows

[1] Ber. d. chem. Ges. **13**, 243. [2] Ztschr. anal. Chem. **8**, 52. [3] Ibid **8**, 398.

it to cool, adds a little water and heats. The liquid is filtered and a solution of sodium nitro-prusside added, and this reacts for sulphur by giving a reddish-violet coloration.

Powdered zinc having the property of decomposing organic substances when heated with them, it seemed that this might be a ready substance to decompose organic bodies, and at the same time to unite with the halogens to form chloride, bromide or iodide, as the case might be, all of which are soluble in water. From the water solution the corresponding silver salt would be precipitated, which would aid to identify the halogen in the substance treated.

The substances containing sulphur in any form of combination would on heating with zinc form zinc sulphide. This could be decomposed by the addition of hydrochloric acid direct to the tube containing the zinc and charred residue of the organic substance, if any, and the sulphuretted hydrogen gas then tested for at the mouth of the tube by means of a narrow strip of filter-paper moistened with lead acetate solution.

The method of procedure outlined was tried on many organic substances containing chlorine, bromine, iodine, and sulphur, and gave the expected results. Several organic substances containing no chlorine, bromine or iodine were treated in the same manner, and a white precipitate invariably appeared on the addition of nitric acid and silver nitrate solution. The distilled water was tested, but gave no reaction for chlorine. A small quantity of zinc was shaken with water, the liquid poured on a filter, and to the filtrate nitric acid and silver nitrate solution were added, and immediately a white precipitate appeared, which was soluble in ammonium hydrate and reprecipitated by nitric acid, showing the presence of a large quantity of chlorine in the zinc. The test for sulphur was made as described, a brown color being obtained on the lead acetate paper, showing the presence of a small amount of sulphur. The zinc was some used in the organic laboratory work, and came in the form of powder. As the zinc used contained chlorine and sulphur, the tests already made were valueless.

Another sample of fine zinc used in the reduction of ferric iron solutions was treated for chlorine and gave no reaction. It also gave no reaction for sulphur. This zinc comes in a spherical form, the diameters of which are mostly half a millimeter. The experiments made with the impure zinc were repeated with the pure sample, and also on several other compounds. The test on

substances containing no chlorine, bromine, iodine nor sulphur were made, and in no case was a distinct reaction obtained. In but one case an opalescence appeared after the addition of nitric acid and silver nitrate solution, while in all the others the solution remained perfectly clear. No trace of sulphur could be detected. This proved that the decomposition of organic substances on heating would not give reactions similar to the ones characteristic of the elements sought.

The substance was heated in about the same manner in every case, with a few exceptions, which will be described. Many of the tests were made in small hard-glass closed tubes, such as are used in blowpipe analysis, having an internal diameter of five millimeters and a length of sixty millimeters. Four-inch test tubes were found to give as satisfactory results.

The exact details of manipulation are as follows:

The substance is first introduced into the tube and then the zinc is added in about equal volume. They are intimately mixed by shaking. The tube is held in a slanting position, with the lower end in the flame, and heated slowly. In many cases the substance volatilises, condenses in the upper end of the tube, and runs down upon the hot zinc, when it is decomposed. In others it carbonises and a watery colored liquid distills.

If combustible gases or vapors are given off, they are lighted. It is better not to heat the tube red hot, for in that case the zinc would melt to a globule and inclose some of the zinc salt formed. At the same time the zinc chloride, bromide and iodide would be volatilised and thus cause a loss. Zinc sulphide is not volatile.

If a liquid is under examination, it is better to use a test-tube, as the mouth is wider. The liquid is first added to the test-tube, which moistens the sides, so that when the zinc is added it will adhere to the inner walls and some remain near the mouth. The test-tube, held in a wooden holder, is slightly heated, and the vapors, if inflammable, are ignited, while the tube is held in a position nearly horizontal. The heat is so regulated that the flame will be as small as possible, and will tend to burn down in the tube and there act upon the zinc adhering to the sides. With the liquids methyl iodide, ethyl iodide and carbon disulphide, this was the only method by which reactions for iodine and sulphur could be obtained. With para-dichlor-benzene this last method gave good results, whereas the general method of heating gave no reaction for chlorine.

After heating with zinc, the residue in the tube is cooled and treated as follows:

For Chlorine.—About one cubic centimeter of distilled water is added direct to the test-tube, the whole shaken and allowed to stand, while a small filter is fitted to a funnel. The liquid is now poured on the filter and caught in a short test-tube placed underneath. The filtrate is acidified with nitric acid and a solution of silver nitrate added. A white precipitate of silver chloride, soluble in ammonium hydrate and reprecipitated by nitric acid, was obtained from the following substances tested:

Liquids.—Chloroform, acetyl chloride, ethylene chloride, allyl chloride.

Solids.—Mono-chlor-crotonic acid, para-di-chlor-benzene, tri-chlor-phenol.

For Bromine.—The contents of the tube are treated with water and filtered, as in the test for chlorine. The filtrate is divided into two parts. In one part nitric acid and silver nitrate solution are added, when the light yellow precipitate of silver bromide appears. To the other part of the filtrate nitric acid is added and a few drops of carbon disulphide. The carbon disulphide is colored brown from the bromine liberated. In several cases the precipitate of silver bromide was very slight, but in every case the carbon disulphide was strongly colored.

The following substances gave the reactions described:

Liquids.—Acetyl bromide, amyl bromide, iso-butyl bromide, brom-toluene.

Solids.—Tribrom-aniline, ortho-nitro-dibrom-phenyl-propionic acid, dibrom-benzene, mono-brom-camphor, di-brom-camphor, eosine, di-brom-gallein, dibrom-anthraquinone, di-brom-anthracene.

For Iodine.—The filtrate is divided and treated as in the case of bromine. Yellow silver iodide is obtained in the first instance, and the carbon disulphide colored violet by the iodine freed from the zinc by the nitric acid in the second.

Iodine was thus detected in the following substances:

Liquids.—[1] Methyl iodide, ethyl iodide, allyl iodide, iso-butyl iodide.

[1] The liquid iodides used were more or less decomposed and colored by iodine set free. In order to work upon undecomposed chemicals, they were each separately shaken with potassium hydrate solution, to take up the iodine, and the resulting colorless alcoholic iodide was repeatedly washed with water. The iodides thus treated were used for the experiments.

Solids.—Iodoform.

For Sulphur.—To the tube containing the residue after heating the substance with zinc, a few drops of hydrochloric acid are added, and the hydrogen sulphide generated identified as it escapes from the mouth of the tube by filter-paper moistened with lead acetate solution. The paper is turned brown almost immediately. There is no necessity for heating the tube. The compounds in the list gave distinct reactions.

Liquids.—Carbon disulphide, allyl mustard oil, ethyl sulphocyanate.

Solids.—Sulpho-urea, potassium amyl sulphate, sulphanilic acid, ammonium di-phenyl-amid-azo-benzene sulphonate, saccharin, sodium beta-naphthol di-sulphonate, mono-sodium anthraquinone sulphonate, morphine sulphate.

It is claimed that, by using the process described, chlorine, bromine, iodine, and sulphur can be accurately and rapidly detected in organic compounds by the use of apparatus and chemicals ordinarily found in chemical laboratories.

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

SPECIFIC VOLUME OF CAMPHOR AND OF BORNEOL DETERMINED WITH PROXIMATE ACCURACY.

BY MITSURU KUHARA.

The materials employed in the experiments were ordinary commercial camphor and borneol, purified by repeated sublimation. Their melting and boiling points[1] were found to be as follows:

	Melting point.	Boiling point.
Camphor,	177.7°	205.3°
Borneol,	...	209.7

In these determinations a number of experiments were repeated, and in each the necessary corrections were made.

The determination of the specific gravity of liquid camphor and of liquid borneol was made with the use of a cylindrical specific gravity bottle of small size, whose capacity had carefully been

[1] In most text-books the melting and boiling points of camphor are given to be 174° and 204° respectively, and the boiling point of borneol to be 212°.

ascertained by filling it with boiled distilled water. Either the camphor or the borneol was fused in a long cylindrical vessel over the paraffin bath, and the specific gravity bottle and its stopper, tied separately with platinum wire, were both introduced into this cylindrical vessel and heated together with the melted camphor or borneol. As the boiling point of the liquid camphor and of the liquid borneol is always found a few degrees higher than that of the vapor, the moment the temperature of the liquid reached 205.3° or 209.7° (boiling points of their vapors), the stopper was instantly closed and the bottle filled with the liquid was taken out, cooled and weighed. These experiments were conducted under a higher barometric pressure than the normal, all the measurements being made by means of the corrected thermometer. The specific gravity was calculated according to the following formula, referring to the water of 4°:

$$\text{Specific gravity} = \frac{W}{V(1+3\beta)(T-t)}.$$

W = Weight of the liquid camphor or borneol at T.
T = Boiling point of camphor or borneol.
V = Volume of water at t (or the capacity of the bottle at t).
t = Temperature when the bottle filled with water was weighed.
3β = Coefficient of the cubical expansion of glass = 0.0000254.

I.—*Experiments on Camphor*, $C_{10}H_{16}O$.

The following three experiments were performed with a bottle of the capacity of 6.28114 cc. at 30.5°.

(1) Camphor in the bottle weighed 5.1304 grams at 205.3°.
(2) " " " 5.1089 " "
(3) " " " 5.1189 " "

The fourth experiment was performed with a bottle of the capacity of 2.98632 cc. at 40.5°.

(4) Camphor in the bottle weighed 2.4252 grams at 205.3°.

Seven more experiments were performed with a bottle of the capacity of 2.74518 cc. at 40.5°.

(5) Camphor in the bottle weighed 2.2400 grams at 205.3°.
(6) " " " 2.2470 " "
(7) " " " 2.2405 " "
(8) " " " 2.2330 " "
(9) " " " 2.2355 " "
(10) " " " 2.2290 " "
(11) " " " 2.2315 " "

Specific gravity at 205.3° deduced according to the formula given above:

(1)	0.8131	(7)	0.8127
(2)	0.8097	(8)	0.8100
(3)	0.8113	(9)	0.8109
(4)	0.8087	(10)	0.8085
(5)	0.8125	(11)	0.8094
(6)	0.8147		

Mean, 0.8110.

$$\text{Specific volume} = \frac{\text{molec. wt.}}{\text{sp. gravity}} = \frac{152}{0.811} = 187.42$$

II.—*Experiments on Borneol,* $C_{10}H_{18}O$.

The experiments were performed with a bottle of the capacity of 2.74518 cc. at 40.5°.

(1)	Borneol in the bottle weighed		2.2284	grams at	209.7°.
(2)	"	"	2.2284	"	"
(3)	"	"	2.2265	"	"
(4)	"	"	2.2245	"	"
(5)	"	"	2.2390	"	"
(6)	"	"	2.2258	"	"

Specific gravity at 209.7°.

(1)	0.8082	(4)	0.8071
(2)	0.8082	(5)	0.8120
(3)	0.8075	(6)	0.8073

Mean, 0.8083.

$$\text{Specific volume} = \frac{\text{molec. wt.}}{\text{sp. gravity}} = \frac{154}{0.8083} = 190.5$$

The specific volume of camphor and that of borneol calculated with Kopp's values of the atomic volumes of carbon, hydrogen, and oxygen, regarding the former as a ketone and the latter as an alcohol, are found to be as follows:

Camphor.			Borneol.		
C_{10}	10×11	$= 110$	C_{10}	10×11	$= 110$
H_{16}	16×5.5	$= 88$	H_{18}	18×5.5	$= 99$
O	1×12.2	$= 12.2$	O	1×7.8	$= 7.8$
Specific volume,		210.2			216.8

Thus it is seen that the calculated values are much greater than those found by experiment. Also the specific volume of benzene and of some of its derivatives, calculated with Kopp's values, is

often found to be much greater than those obtained experimentally. In Watts' Dictionary of Chemistry, 3d Supplement, page 2126, the following statements are given: "Lothar Meyer makes H = 3, and Löschmidt C = 14 and H = 3.5; and by assuming that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value 3.5, we obtain a value for this hydrocarbon which is identical with the observed values." Thus:

	Calculated.		Found.	
			Kopp.	Ramsay.
C_6	$3 \times 14 = 42$	96	95.8	95.9
C_5	$3 \times 11 = 33$			
H_6	$6 \times 3.5 = 21$			

I tried to apply these values of carbon and hydrogen and Kopp's values of oxygen (12.2 and 7.8) to camphor and borneol, supposing each to consist of a closed chain of six carbon atoms like benzene, and I found that the calculated specific volumes are almost concordant with those observed.

Camphor.			Borneol.		
	Calculated.	Found.		Calculated.	Found.
$C_6 = 3 \times 14$	187.2	187.42	$C_6 = 3 \times 14$	189.8	190.5
$C_7 = 7 \times 11$			$C_7 = 7 \times 11$		
$H_{16} = 16 \times 3.5$			$H_{18} = 18 \times 3.5$		
$O = 1 \times 12.2$			$O = 1 \times 7.8$		

I tried further to compute the specific volumes of some of the benzene derivatives whose experimental numbers are already known by applying a similar method of calculation to them, thus:

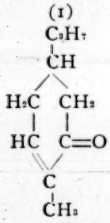
	Found.			Calculated.	
	Kopp.	Ramsay.	Yoshida.	C = 14 & 11; H = 3.5; O = 12.2 & 7.8.	C = 11; H = 5.5; O = 12.2 & 7.8.
Benzene,	95.8	95.9	...	86.0	99.0
Phenol,	103.6	106.9	...	103.8	106.9
Benzyl alcohol,	123.7	...	..	121.8	128.8
Benzaldehyde,	118.4	...	...	119.2	122.2
Ethyl benzoate,	172.4–174.8	...	163.1[1]	162.0	174.0
Benzoic acid,	126.9	...	...	127.0	130.0
Naphthalene,	149.2	...	...	150.0	154.0

It thus appears that the numbers found by the new way of calculation agree better with the observed ones in some cases than with those calculated with Kopp's values.

[1] This number was observed according to Ramsay's method by Mr. H. Yoshida, Science College, Imperial University of Tokio.

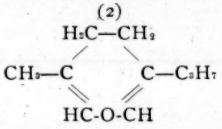
Now, the principal formulæ for camphor suggested by different chemists are six in number, namely:

(1)



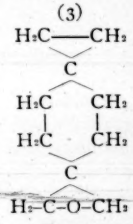
Kekulé.

(2)



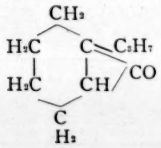
Victor Meyer.

(3)



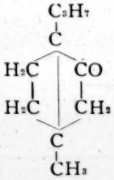
Hlasiwetz.

(4)



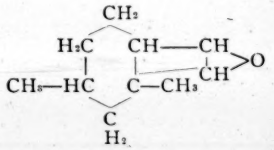
Kachler.

(5)



Kanonnikow.

(6)



Armstrong.

If we suppose the above method of calculation to be true, there may exist in camphor a closed chain of six carbon atoms, and camphor itself may be a ketone, and then the formula 1, 4 or 5 may represent its constitution, as any one of the remaining formulæ would represent it as an oxide. Kanonnikow,[1] however, who determined the refraction equivalent of camphor and of its allied compounds by applying Brühl's method, states that camphor has no double union between carbon atoms. Hence, it may be concluded that one of the formulæ 4 and 5 represents the constitution of camphor, and borneol is its corresponding alcohol.

Chemical Laboratory, First Kôto-chiu-Gakko, Tokio, Japan, *July*, 1888.

(1) Ber. d. chem. Ges. **6**, 929.
(2) Ibid. **3**, 116.
(3) Ibid. **3**, 540.
(4) Ann. Chem. (Liebig) **165**, 185.
(5) Ber. d. chem. Ges. **16**, 3051.
(6) Ibid. **11**, 1698.

[1] Ber. d. chem. Ges. **16**, 3051.

A RAPID COLORIMETRIC METHOD OF DETERMINING NITRATES IN POTABLE WATERS.[1]

By Samuel C. Hooker.

[Read at the Stated Meeting of the Chemical Section of the Franklin Institute, March 19, 1889.]

In devising a process for the estimation of nitrates in the minute quantities in which they occur in natural waters, I have not been ignorant of the fact that there are already several very satisfactory ways in which this can be accurately done. I have, however, aimed at greater rapidity than has heretofore been possible.

Fully fifteen years ago, Graebe and Glaser discovered carbazol, and observed that when dissolved in concentrated sulphuric acid, it gave rise to an intensely green solution on the addition of nitric acid. This reaction, which up to the present time has been used only as a means of identifying carbazol, forms the basis of the process to be described. Its extraordinary delicacy renders it particularly suitable for the purposes of water analysis, and enables a quantity of nitric acid, containing as little as $\frac{6}{100000}$ of a milligram of nitrogen, to be accurately determined. The reaction is not, however, peculiar to nitric acid; all oxidising agents behave similarly. Graebe and Glaser enumerate chlorine, bromine, iodine, nitrous and chromic acids as giving rise to the same intensely colored solution. With the exception of nitrous acid, the substances just mentioned are almost invariably absent from natural waters, and may therefore be dismissed from further consideration. There is, however, one other oxidising agent, namely iron in the ferric condition, which is sometimes found in very appreciable quantities, and it therefore became necessary, in studying the influence of the substances in solution upon the process, to give special attention to iron as well as to nitrous acid.

As the result of a number of careful experiments, the following conclusions were arrived at with regard to the application of the process:

(1) No material error will arise in the presence of nitrites in the quantities in which they usually occur.

(2) Iron (in the ferrous or ferric condition), if present in quantities greater than 0.1 part per 100,000, must be removed.

[1] See preliminary paper, Journal of the Franklin Institute **127**, 61. Ber. d. chem. Gesell. **21**, 3302.

(3) Chlorides, even when present in very small quantities, must be removed.

(4) Carbonate of lime, sulphates of lime, soda, etc., in the quantities in which they ordinarily occur, were not found to influence the determinations.

(5) The presence of easily destructible organic matter, such as albumen, lowers the result; not materially, however, unless present in large excess.

The estimation, briefly described, is made as follows:

Two cubic centimeters of the water to be examined is mixed with 4 cc. concentrated sulphuric acid; the mixture is cooled, and a small quantity of carbazol, dissolved in sulphuric acid, added. If nitric acid is present, the solution will turn green on the addition of the carbazol; and the intensity of the color, by comparison with that produced by solutions of potassic nitrate of known strength, will, within certain limits, indicate the amount of the acid present.

The great majority of waters can be estimated directly without previous concentration, and only a few will need to be diluted. The limits within which the determinations may be safely made are marked by quantities of nitric acid represented by .03 and .40 part N per 100,000. Water containing either less or more nitric acid than indicated by these figures must be concentrated or diluted.

To test the accuracy of the process, a number of solutions were prepared, at my request, containing different quantities of potassic nitrate. In order that my judgment might not be influenced by a knowledge of the amount of nitric acid present, I was kept in ignorance of the strength of the solutions until after the estimations had been completed.

The following are the results obtained:

Nitric Acid expressed as N *in Parts per* 100,000.

Present.	Found.	Error.
.127	.130	+ .003
.078	.075	— .003
.200	.190	— .010
.302	.300	— .002
.290	.290	.000

Average error, ...0036

Nitric Acid present in the 2 cc. of Water operated upon, expressed in Decimals of a Gram.

Present.	Found.	Error.
.00001143	.00001170	.00000027
.00000720	.00000675	.00000027
.00001800	.00001710	.00000090
.00002718	.00002700	.00000018
.00002610	.00002610	.00000000
Average error, ...		.000000324

The above results are not selected, but include all the determinations that have been made with solutions of unknown strength, with the object of testing the delicacy of the process. It is to be borne in mind that potassic nitrate *only* was present. Considering the extremely minute quantities operated upon, the accuracy of the above results is very noteworthy.

The following reagents are required:

(1) Concentrated sulphuric acid.

(2) An acetic acid solution of carbazol.

(3) A sulphuric acid solution of carbazol.

(4) Standard solutions of potassic nitrate.

(5) A solution of aluminic sulphate.

(6) A solution of sulphate of silver.

(1) The sulphuric acid, used for all purposes in the process, should be almost entirely free from oxides of nitrogen. It may be readily tested by dissolving in it a small quantity of carbazol. If the solution be at first golden yellow or brown, the acid is sufficiently pure; if it be green or greenish, another and better sample must be taken. It is essential also that the specific gravity of the acid be *fully* 1.84, and it is well to ascertain that this is really the case, as I have found several samples, obtained from sources which are generally thought reliable, to fall considerably below these figures. The acid was in fact worthless for the purpose required. As the success of the process depends upon the proper strength of the acid, I cannot lay too much stress upon this point.

(2) The carbazol used was obtained from Kahlbaum,[1] of Berlin. The acetic acid solution is prepared by dissolving 0.6 gram in about 90 cc. of 99–100 per cent. acetic acid, by the aid of gentle heat. It is allowed to cool, and is then made up to 100 cc. by the

[1] Kahlbaum's carbazol may be obtained from James W. Queen & Co., Philadelphia.

further addition of acetic acid. The exact strength of this solution is of no material importance to the success of the process, and the above proportions have been selected principally because they are convenient. The solution will probably remain unchanged almost indefinitely; but I cannot speak positively in this respect, as my actual experience extends only over a period of several months. The use of this solution merely facilitates the preparation of that next described, which will not keep, and has consequently to be freshly prepared for each series of determinations.

(3) The sulphuric acid solution of carbazol is easily made in a few seconds, but it is advisable to allow it to stand from one and one-half to two hours before using. It is prepared by rapidly adding 15 cc. of sulphuric acid to 1 cc. of the above described acetic acid solution. This quantity usually suffices in my hands for from two to three nitrate estimations. When freshly prepared it is golden yellow or brown; it changes gradually, however, and in the course of one and one-half or two hours it becomes olive-green. I am not able to say positively to what this change is due, but it seems probable that traces of oxidising agents occur in the sulphuric and acetic acids, and that these, although not present in sufficient quantity to act immediately, gradually bring about the reaction described. The greenish color does not interfere with the process, as might at first be supposed; on the contrary, I have observed that the solution is not sensitive to small quantities of nitric acid until it has undergone the change to olive-green, and it is for this reason that I have advised that it should be prepared about two hours before required for use. This solution may be thoroughly depended on for six hours after preparation. The intensities of color produced by the more concentrated solutions of nitrates after this time, gradually approach to each other and become ultimately the same.

(4) The standard solutions of potassic nitrate are very readily prepared. The solutions which are to be compared directly with the waters examined, may be prepared as required, but if many determinations are to be made with a variety of waters, it will be found best to prepare a complete series, differing from each other by .02 part nitrogen in 100,000. This series may include solutions containing quantities of nitrogen in 100,000 parts, represented by all the odd numbers from .03 up to .39. It will be found convenient to prepare them in quantities of 100 cc. at a time, from a stock

solution of potassic nitrate (b) which contains .00001 gram nitrogen, or .000045 nitric acid in 1 cc. Each cubic centimeter of this solution, when diluted to 100 cc., represents .01 nitrogen in 100,000, and consequently if it is desired to make a solution containing .35 part nitrogen in 100,000, 35 cc. are taken and made up to 100 cc., and so on. The solution of potassic nitrate (b) is best prepared from a stronger one (a) containing .0001 gram nitrogen to the cubic centimeter, or .7214 gram potassium nitrate to the liter: 100 cc. of (a) made up to one liter gives the solution (b). It is obvious that the series of solutions above described could be made directly from (a), but by first making (b), greater accuracy is secured.

(5) For purposes which will be presently described, a solution of aluminic sulphate is required, containing five grams to the liter. The salt used must be free from chlorine and iron; and the solution should give no reaction when tested, as in the case of a water with carbazol.

(6) The solution of sulphate of silver is required for the removal of chlorine from the water to be examined. It is prepared by dissolving 4.3943 grams of the salt in pure distilled water and making up to one liter. The sulphate is preferably obtained by dissolving metallic silver in pure sulphuric acid. The solution should be tested with carbazol in the same way as will be presently described for water; if perfectly pure, no reaction will be obtained. As sulphate of silver is often prepared by precipitation from the nitrate, it is very apt to contain nitric acid, and consequently, if the source of the salt be not known, this test should on no account be omitted.

Having described the preparation of the reagents, the method of making the determinations may now be considered more in detail. Assuming the water to be free from all substances capable of affecting the accuracy of the results, the process is carried out as follows: Two cubic centimeters of the water is carefully delivered by means of a 2 cc. pipette into the bottom of a test-tube; 4 cc. of sulphuric acid is added, and the solution thoroughly mixed by the help of a glass rod. The test-tube is then immersed in cold water, and when well cooled, 1 cc. of the sulphuric acid solution of carbazol is added, and the whole again mixed as before. The intensity of the color is now observed, and a little experience enables a fairly good opinion to be formed of the quantity of nitric acid present. Suppose that the water is roughly estimated

to contain about .15 part nitrogen per 100,000, in such a case, solutions of potassic nitrate containing .11, .15, .19 part nitrogen are selected from the series. Two cubic centimeters are taken from each, and treated side by side with a fresh quantity of the water, precisely as described for the preliminary experiment; the various operations being performed as nearly simultaneously as possible with each of the samples, and under precisely similar conditions. Two or three minutes after the carbazol has been added, the intensity of the color of each is observed. If that given by the water is matched by any of the standard solutions, the estimation is at an end. Similarly, if it falls between two of these, the mean may be taken as representing the nitrogen present in cases in which great accuracy is not required. If this be done, the maximum error will be .02 nitrogen, or .09 part nitric acid per 100,000. If greater exactness be required, or it be found that the color given by the water is either darker or lighter than that given by all the standard solutions, a new trial must be made. In such a case the water must be again tested simultaneously with the solutions with which it is to be compared. This is rendered principally necessary for the reason that the shade of the solutions to which the carbazol has been added is apt to change on standing. Hence it is desirable that the water, and the standard potassic nitrate with which it is to be compared, should have the carbazol added at as nearly the same time as possible. When finally the color falls between that given by any two consecutive members of the standard potassic nitrate series, the estimation may be considered at an end, and the mean of these solutions taken as representing the nitrogen present. The maximum error in this case will be only .01 nitrogen per 100,000 parts, and the mean error slightly more than .005. This degree of accuracy is believed by the author to be quite sufficient for, if indeed it does not exceed the needs of, all ordinary cases of water analysis for sanitary purposes, for which the process was specially devised. If occasionally, however, greater accuracy is desirable, the determinations recorded in the early portion of this paper show that the average error can be reduced to .0036 part nitrogen per 100,000. In this case the standard solutions employed must differ from each other by .01 part nitrogen only. The additional accuracy gained, however, will scarcely repay for the extra time, care and labor required, and even in this case, as will be seen by a reference to the above determinations, the error may amount to .01 part nitrogen per 100,000.

In the course of a great many experiments I have observed, even when the utmost care has been taken, that two solutions, nominally containing the same amount of nitric acid, occasionally give a very slight though distinctly perceptible difference in shade when tested side by side. Whatever may be their cause, such differences are extremely slight, and if proper care be taken, do not materially affect the value of the process.

I cannot too strongly insist upon the necessity of scrupulous cleanliness at all stages of the analysis. The quantity of water operated upon is so small, that if the greatest care be not exercised throughout, sources of considerable error may be readily introduced. The test-tubes used in the process may be conveniently 5 x $\frac{8}{8}$ inches in size. They should, of course, be as nearly the same in diameter as possible. It is scarcely necessary to add that they should always be dry when used, and rinsed out carefully with distilled water when put aside.

In comparing the color given by a water with that produced by standard potassic nitrate, it is necessary only to examine the solutions *through* the tubes; differences in shade which can only be detected by looking through the length of the columns of liquid, may be disregarded. It is well to use the same 2 cc. pipette for measuring both the water and the standard potassic nitrate; the effect of any error in graduation is thus neutralised.

I have made experiments to ascertain whether the intensity of color produced is strictly proportional to the nitric acid present, with a view to render the use of a colorimeter possible, and thus to avoid the time and trouble necessary to match the colors given by the waters. The result of these experiments, which were made with a Duboscq instrument, shows conclusively that the changes already referred to in both tint and intensity after the addition of the carbazol, occur more rapidly with the light than with the dark solutions, and hence they are not strictly comparable.

Influence of Nitrites.

It has been already pointed out that nitrous acid behaves similarly to nitric acid in its action on a sulphuric acid solution of carbazol. In order to estimate to what extent its influence would be felt when present in the water to be examined for nitrates, several solutions of silver nitrite were carefully prepared and estimated precisely as if they contained a nitrate.

The results obtained are given in the following table:

Results expressed as N *in* 100,000 *Parts.*

Present as $AgNO_3$.	Found.	Error.	Corrected by deducting one-fifth from amount found.
.10	.12	.02	.096
.20	.25	.05	.200
.30	.37	.07	.296

It will be observed that the error may be very nearly corrected by deducting one-fifth from the amount found. In the presence of nitrates, this correction, of course, will only be possible in cases in which the quantity of the nitrous acid present has been previously ascertained. A correction, however, would be rarely necessary.

Influence of Iron.

Although a solution of ferrous sulphate gives no reaction with carbazol, nitrates are apt to be overestimated in the presence of iron in the ferrous condition. Ferric salts, however, acting like other oxidising agents, are themselves able to give the characteristic green color with carbazol. I have made a number of experiments with solutions of potassic nitrate in the presence of both Fe″ and Fe‴ in varying amounts, and have ascertained that if iron be not present in quantities greater than 0.1 part per 100,000, the error will not exceed .01 part in 100,000. The condition of a water with regard to iron may be ascertained sufficiently accurately in a few seconds by the help of ammonic sulphide. As this is a test which should always be made in the examination of water for sanitary purposes, no extra trouble is involved. In a case in which iron is present in large quantities, it can be easily eliminated by rendering the water slightly alkaline, evaporating to dryness, and redissolving the soluble residue in the same volume of pure distilled water as was taken of the water under examination.

Influence of Chlorides.

Chlorides form by far the most serious source of error in this process, by intensifying the action of the nitric acid. If, however, nitrates be absent, chlorides give no reaction with carbazol. Were it not for the fact that the chlorine can be perfectly removed in the space of a very few minutes, the general usefulness of the method

would be much restricted. In order to remove the chlorine I use the standard sulphate of silver already referred to, 1 cc. of which, when consumed by 100 cc. of water, is equivalent to one part of chlorine in 100,000 parts of water. Having first determined the chlorine present, by means of a standard nitrate of silver solution of equivalent strength, the exact quantity of sulphate of silver required is known. I proceed as follows: A flask, graduated on the neck at 100 cc. and 110 cc., is filled up to the 100 cc. mark with the water to be examined. The necessary quantity of sulphate of silver is next added, and then 2 cc. of the solution of aluminic sulphate previously described; finally, the contents of the flask are brought up to the 110 cc. mark by the addition of pure distilled water. The whole is shaken up and filtered; the first portion of the filtrate, which will contain any foreign substances derived from the filter paper, is thrown away. The aluminic sulphate, by reacting with the carbonates usually present in the water, and thus giving rise to the precipitation of alumina, facilitates the removal of the precipitated chloride of silver, which otherwise, under the conditions given above, is extremely difficult to separate, and may even still pass through the paper after refiltering many times. When the filtrate is perfectly bright, a portion is tested to make sure that all the chlorine is removed; the estimation is then made precisely as already described, the amount found being increased by one-tenth to compensate for the dilution of the 100 cc. of the water taken to 110 cc.

It is obvious that such a flask as I have described cannot be used in cases in which the chlorine exceeds eight parts per 100,000, unless the sulphate of silver solution be of greater strength than that which I have recommended. Similar methods will, however, readily suggest themselves.

In a preliminary paper[1] published on this process, I mentioned that probably diphenylamine, and other compounds giving similar color reactions in the presence of concentrated sulphuric acid, might be used instead of carbazol for the *quantitative* estimation of nitrates in water. Shortly after this paper appeared, L. Spiegel[2] called attention to a process worked up by him, in which diphenylamine was actually used for this purpose. This is briefly described in the *Zeitschrift für Hygiene*, 1887, 2, 189, and was quite unknown

[1] Ber. d. chem. Gesell. **21**, 3302; Journal of the Franklin Institute **127**, 61.
[2] Ber. d. chem. Gesell. **21**, 3568.

to me. Although differing in detail from that which I have devised, the principle is the same, diphenylamine taking the place of carbazol. Spiegel does not mention any experiments made to ascertain the influence of chlorides, but it is probable that this will be found as considerable as I have found it in the case of carbazol.

THE DISSOCIATION OF THE OXIDES OF ZINC AND CADMIUM IN THE VAPORS OF THEIR RESPECTIVE METALS.

By H. N. Morse and J. White, Jr.

Thirty-four years ago, St. Claire Deville[1] heated some pure oxide of zinc in a porcelain tube, through which a slow current of pure and dry hydrogen was passing. At some distance from the original material he obtained deposits of fine and often large crystals of the oxide. At first he ascribed this transportation of the material to sublimation, and concluded that the oxide is not reducible in a current of hydrogen. But, having learned of the production of metallic zinc in the same way by Rivot, he was led to construct a new explanation for the apparent volatility of zinc oxide in a current of hydrogen. He supposed that the oxide is reduced by the hydrogen, with formation of water and metallic zinc; these then pass along the tube together, until a place having a higher temperature is reached, when the vapor of the metal decomposes the water, with formation of zinc oxide and free hydrogen. This explanation appears to have been accepted as sufficient by all.

On comparing his own apparatus and procedure, by which deposits of oxide only were obtained, with the apparatus and procedure of Rivot, who obtained the metal, it appeared that the latter employed a narrower tube and a much more rapid current of hydrogen. It was afterwards found that, by appropriately varying the width of the tube, the quantity of the oxide, and the rapidity of the current of hydrogen, he could obtain deposits of oxide, of oxide and metal, or of metal and a minute quantity of oxide.

[1] Ann. chim. phys. (3), **43**, 7 and 477.

Eleven years later, Deville and Troost[1] described an exactly analogous transportation of the sulphides of zinc and cadmium. These were heated in porcelain tubes, in a slow current of pure hydrogen, and, as in the case of the oxide, they were afterwards found some distance away as deposits of hexagonal crystals. To prove that the volatility of the sulphides is only apparent, they were heated to the highest attainable temperature, in a current of hydrogen sulphide. No trace of sublimation could be discovered. The explanation given by the authors is identical in principle with that previously given for the apparent volatility of the oxide. The sulphides were supposed to have been reduced by the hydrogen, with formation of sulphide of hydrogen and free metals. These then passed along together to some other portion of the tubes, where the metallic vapors recovered their sulphur by displacing the hydrogen of the sulphide of hydrogen.

The theory of Deville to explain these interesting phenomena presents certain difficulties. In the first place we must assume a very considerable change in the relative affinities of oxygen and sulphur for hydrogen on the one hand, and the zinc on the other. This would involve large differences of temperature in different parts of the tube; such differences, in fact, as are not likely to have existed under the circumstances of the experiments. Deville speaks of the depositions as having occurred in the hotter portions of the tubes, but we infer from the fact that he obtained deposits which were mixtures of oxide and *metal*, that the places of deposition were certainly not hotter than those from which the metal was first distilled. Again, the sulphide of hydrogen begins to dissociate at 400°, and is destroyed by passing it through a porcelain tube heated to redness. It appears probable, therefore, that the sulphide of hydrogen was not formed at all during the experiments in which the sulphides of zinc and cadmium were transported.

These phenomena are susceptible of quite another explanation than that given by Deville, for which we are able to give some experimental evidence in the dissociation of the oxides of zinc and cadmium in the vapors of their own metals. We suggest that the transportation of the oxide of zinc and the sulphides of zinc and cadmium in a current of hydrogen may have been due to a *dissociation* of the original compounds under the influence of the excess of hydrogen, with reformation at other points where the hydrogen,

[1] Ann. chim. phys. (4), **5**, 118.

owing to its deficiency of quantity or lack of temperature, was no longer able to prevent the union of the oxygen and sulphur with the metals. If the chemical elements exert their mutual attractions at other temperatures and under other conditions than those which permit of their actual combination, as we are forced to infer from certain phenomena classed under the heads of *mass* and *catalytic* action, it appears to follow that, when two substances, one a compound and the other something which has an affinity for one of the constituents of the same, are brought together, the stability of the compound must be diminished so that it will dissociate at lower temperatures than in the absence of the substance which exerts an attraction upon one of its constituents. The following three equations will serve to make the meaning of the statement somewhat clearer:

1. $AB + A = A + A + B.$
2. $AB + B = A + B + B.$
3. $AB + C = A + B + C.$

AB is supposed to represent any compound, *e. g.* ZnO; if now, as in the first and second equations, AB is treated with one of its own constituents in the free state, the added substance, owing to its attraction for the other constituent of the compound, should render the compound less stable, and therefore susceptible of dissociation at lower temperatures.

Again, the stability of the compound should be diminished by the presence of a substance, not in it, but having an affinity for one of its constituents, as represented in the 3d equation.

We have already demonstrated two cases falling under the first equation, by showing that the oxides of zinc and cadmium can be readily dissociated in the vapors of their respective metals.

The third equation represents what we suppose to have taken place in the experiments of Deville and of Deville and Troost. If the oxide of zinc is heated in a current of hydrogen, it is quite possible that, owing to the attraction of the hydrogen for the oxygen, the oxide may be made to break up into its constituents. These would then travel along the tube together, except so far as they separated in consequence of different rates of diffusion, and recombine whenever the attraction of the hydrogen for the oxygen no longer sufficed to keep them separated. Such a failure of the hydrogen to maintain the dissociated condition of the zinc and

oxygen might result from a lessening of its relative quantity, or from a lowering of the temperature. The latter appears to be the more probable cause of the reunion of the zinc and oxygen. In the same way the sulphides of zinc and cadmium in a current of hydrogen might be dissociated into their elements, which would volatilise and recombine whenever the conditions permitted.

It is not necessary to suppose the intermediate formation of water in the first case, nor of sulphide of hydrogen in the second. Indeed, the formation of the latter unstable compound appears to be quite improbable.

In order to test experimentally the view here presented, we have selected two of the simplest possible cases falling under the first equation: the dissociation of the oxide of zinc by metallic zinc, and of the oxide of cadmium by metallic cadmium. It has been proved[1] that, under the pressure of the atmosphere, the oxide of zinc does not dissociate below the fusing point of steel, approximately 1400°. But in this work it was decided to experiment, if possible, in a vacuum, because it appeared probable that, should dissociation take place, a portion of the oxygen, owing to its more rapid diffusion, could be isolated, and thus the fact of dissociation demonstrated beyond question. Hence it was necessary to first test the stability of the oxides of zinc and cadmium in a vacuum. This was done by placing them in hard glass tubes closed at one end, and drawing out the open ends so as to properly connect with a Sprengel pump. The tubes were then exhausted, and afterwards heated in a combustion furnace until the glass softened and collapsed from external pressure. During the heating the pump was kept in operation, and a tube filled with mercury maintained over the outlet in order to collect any gas which might be liberated from the oxides. No oxygen was obtained, neither did the oxides exhibit any signs of volatility. It was therefore concluded that they are stable in a vacuum to the highest temperature which we should subsequently employ.

The dissociation of the oxides by means of their respective metals was then effected in the following manner. Hard glass tubes, having a length of about 900 and an internal diameter of about 15 millimeters, were cleansed and closed at one end. The oxides and the metals with which they were to be heated were placed in the closed ends, and any material clinging to the glass

[1] Morse and Burton, this Journal **10**, 319.

above the mixture removed. About one-third of the length of the tube away from the closed end, a deep indentation of the bottom of the tube was made, by softening the glass in the blast-lamp and pressing upon it with a hot triangular file. This was done to prevent any flowing of the metal from the back towards the front end. The open ends were then drawn out and attached by means of rubber tubing, tied with shoemaker's waxed thread, and surrounded by mercury jackets, to a Sprengel pump. The tubes were exhausted to the highest possible degree, and afterwards heated throughout two-thirds of their length, in a combustion furnace. A gas tube filled with mercury was placed over the outlet, after exhaustion had been effected, and the pump kept in operation during the entire experiment. We describe what took place in the case of the zinc oxide and metallic zinc. Very soon after the metal had fused, a fall of several millimeters in the barometer attached to the pump was observed. At the same time gas began to collect in the eudiometer placed over the outlet. On exposing the tube in the furnace to view, it was found that a deposit of yellow oxide had formed in front of the dam. This deposit continued to increase in depth, and to extend itself toward the front end of the tube, until a portion of the zinc had also distilled over and condensed in front of the dam. The oxide which had been deposited near the dam then disappeared, and its disappearance was followed by a rapid increase of the deposition still farther forward. The oxide was thus gradually driven before the distilling zinc, until all of it had been transported to the cool third of the tube lying between the furnace and the pump. In this position it could be seen to fall from above upon the bottom of the tube, in the form of a fine mist of crystals, as long as any zinc remained behind the dam with the oxide not yet dissociated. When all of the zinc had distilled over the dam, and all of the oxide in the heated portion of the tube in front of the dam had been expelled, that is, when metal and oxide were no longer in contact, the deposition at the front end ceased. It could be reinstated, however, by cooling the rear end of the tube, so as to allow the metal to distill back, and then heating again as before. The gas which collected in the eudiometer proved to be pure oxygen. It was measured and determined each time by absorption in an alkaline solution of pyrogallic acid. As would be expected, the collection of the oxygen was most rapid during the early part of the experiment, while the tube

was still comparatively free from the vapors of the metal. The evolution continued, however, throughout the whole experiment.

We give below the weights of oxide and zinc taken, the weight of transported oxide collected in the front end of the tube, and the volume of oxygen isolated :

	Weight ZnO.	Weight Zn.	Weight ZnO (transported).	Volume O_2.
1.	25 grams	44 grams	3 grams	7.1 cc.
2.	18	35	8	11.0
3.	31	50	10	not determined

The above results cannot be considered as in any way comparable with one another, because of the impossibility of regulating the temperature so as to secure identical conditions. It still remains to determine in what manner the dissociation is affected by varying the temperature and the relative proportions of oxide and metal.

The phenomena which presented themselves when the oxide of cadmium was heated with metallic cadmium were essentially the same. The oxide collected in front of the dam was driven from that position by the distilling metal, and finally deposited in the cool portion of the tube, in the form of a brown crystalline powder. The quantities of dissociated oxide and of free oxygen obtained were much less than in the experiments with zinc. This is to be ascribed, in part at least, to the lower temperature and greater rapidity of the distillation of the metal away from its oxide. Two experiments were made. In both of them, 20 grams of cadmium and 10 grams of oxide were employed. In the first case, 1½ grams of dissociated oxide and 3.7 cc. of oxygen were obtained; in the second, 2½ grams of oxide and 1.4 cc. of oxygen. There appears to be but one sufficient explanation for the phenomena here described. The atoms of the free metal attract the oxygen in combination to such an extent that the oxide becomes unstable and dissociates. So long as the conditions under which the dissociation was effected are maintained, reformation of the oxide is impossible; that is, no one portion of the metal will be able to appropriate and hold the oxygen in spite of the rest, and the elements will remain in the free state. But as soon as the attraction of the metal for the oxygen becomes sufficiently diminished by falling temperature, or weakened by distribution over a larger number of oxygen atoms, the recombination takes place.

We shall continue to investigate such cases as appear to be suitable tests of the view here presented.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

THE ELECTROLYTIC METHOD APPLIED TO MERCURY-SEPARATION FROM COPPER.

By Edgar F. Smith and Lee K. Frankel.

The electrolytic precipitation of mercury has been successfully performed by different chemists; thus J. B. Hannay[1] recommends a solution of mercury sulphate for this purpose, but gives no quantitative results. F. W. Clarke[2] separated mercury from the solution of its chloride, feebly acidulated with sulphuric acid, by using a current obtained from six Bunsen chromic acid cells. Classen and Ludwig[3] employed a mercury solution rendered slightly acid with nitric acid, and a current affording .5–1.0 cc. electrolytic gas per minute. The time occupied in the deposition, at ordinary temperatures, was 12–16 hours. Hoskinson[4] obtained good results with the nitrate. Smith and Knerr[5] employed a nitrate solution in which there was considerable acid in excess, and with a current yielding 4 cc. electrolytic gas per minute, deposited .1 gram of mercury in forty-five minutes. In all of these methods which permit of the separation of mercury from many other metals, the mercury is thrown out as a mirror-like deposit, and drops of metal are plainly discernible.

We have observed that this metal can be separated without difficulty from solutions containing a large excess of an alkaline cyanide, and with a comparatively weak current. The solution used was the chloride. The conditions, time, strength of current, and results are as follows with mercury alone:

Solution contained Hg.	Found Hg.	Per cent. difference.	Quantity of KCN.	Total dilution.	Time in hours.	Current in cc. OH gas per minute.
.1945 gram.	.1953	+.41	.26 gram.	175 cc.	16	.2 cc.
	.1948	+.14	"	"	"	"
	.1946	+.05	1.3	"	24	"
	.1930	—.77	"	"	"	"
	.1945	...	"	"	12	"
	.1945	...	"	"	"	"
	.1945	...	2.6	"	"	"
	.1944	—.05	.65	"	"	"
	.1942	—1.4	"	"	"	"
	.1956	+.56	"	"	"	"
	.1957	+.61	1.30	"	"	"
	.1948	+.14	"	"	"	"

[1] Ber. d. chem. Ges. **6**, 270. [2] Am. Journal of Science **16**, 200; and Ztschr. anal. Chem. **18**, 103.
[3] Ber. d. chem. Ges. **19**, 323. [4] This Journal **8**, 209. [5] Ibid.

The deposits in these determinations were compact, rather gray in color, and showed in few cases the drop-like nature so characteristic of mercury.

For washing purposes it was found best to use water only, because when this was followed with alcohol we noticed that the latter detached thin films of metal, causing loss in consequence. The heat of the hand is sufficient to dry the deposit, though a warm iron plate may be used. Some of the deposits were allowed to dry slowly over sulphuric acid. In our experience with about one hundred mercury depositions, we observed but five in which there was a slight oxidation of the metal. This only occurred when a film of water remained in contact for some time with the deposited mercury.

In working with copper solutions, under conditions similar to those mentioned above, we discovered that this metal would not separate until the alkaline cyanide had completely decomposed. We therefore undertook a series of experiments with solutions containing both mercury and copper, hoping to effect their electrolytic separation. This seemed advisable, as the attempts in this direction had thus far not been as successful as might be desired.[1]

Our mercury solution contained the same quantity of metal as in the first experiments. Seventy per cent. of copper was added in each case. The quantity of cyanide varied from .65 gram to 3.9 grams. The total dilution was 200 cc., and the current strength varied from .1–.4 cc. electrolytic gas per minute; time, 6–18 hours. Ten experiments were performed, and notwithstanding the mercury was completely deposited, slight quantities of copper were likewise thrown out of solution.

Thirty additional experiments were made; in each the quantity of mercury was .1945 gram, while the copper varied from 14 to 70 per cent. The quantity of alkaline cyanides varied from 3.9–8.5 grams; total dilution removed 200 cc. The current averaged .4 cc. to 1.2 cc. electrolytic gas per minute; time, 18 hours. The best results were these:

Hg taken.	Hg found.	Diff. in per cent.	Hg found.	Diff. in per cent.
.1945	.1932	— .66	.1936	— .46
	.1920	— 1.28	.1954	+ .46
	.1927	— .92	.1938	— .36
	.1936	— .46	.1923	— 1.13
	.1930	— .77	.1921	— 1.23

[1] Luckow, Ztschr. anal. Chem. **8**, 24; and Classen, Ber. d. chem. Ges. **17**, 2467, and **24**, 247.

These, as well as the results obtained in twenty experiments made later, seem to indicate that the presence of copper exercises considerable influence upon the precipitation of the mercury, in the way of retarding it. This fact, we think, was confirmed by ten more experiments, in all of which a slight portion of the mercury was retained in solution, notwithstanding the current was increased to 1.2 cc. electrolytic gas per minute and the amount of cyanide considerably reduced. The time of each precipitation was continued through seventeen hours.

Our attention was next directed to ascertaining whether or not a stronger current might be used to throw out the mercury and at the same time leave the copper in solution. The results with mercury alone were:

Hg present.	Hg found.	Diff. in per cent.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.
.1833	.1827	—.27	1.5	200 cc.	2.8 cc.	16
	.1832	—.05	"	"	"	"
	.1834	+.05	"	"	"	"

Using the same quantity of mercury and varying amounts of copper, the results were as follows:

Hg present.	Per cent. of copper present.	Hg found.	Diff. in per cent.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.
.1833	1	.1821	—.65	1.5	200 cc.	3.2 cc.	16
	10	.1828	—.27	"	"	"	"
	1	.1821	—.65	"	"	"	"
	14	.1833	...	"	"	"	"
	10	.1821	—.65	"	"	"	"
	5	.1819	—.76	"	"	"	"
	3	.1815	—.98	"	"	"	"
	5	.1834	+.05	"	"	"	"
	3	.1836	+.16	"	"	"	"

The results are recorded in the order obtained, and while the differences in percentage from that required vary from +.05 to —.98, and in six cases out of nine show a deficiency in the mercury, yet a careful qualitative examination of each filtrate failed to detect this metal. The error must, therefore, be ascribed to other causes. It may not be improper to add that these determinations and separations were not always conducted in the same platinum vessels, and further, those used by us ranged in weight from 61–135 grams. Where the quantity of copper exceeded 20 per cent. of the mercury, the results were unsatisfactory.

It is well known that silver can be separated quantitatively from its cyanide solution, but whether its separation from copper could be effected in the same manner as that by which copper and mercury were separated has not been determined. To ascertain this we made forty experiments, ten of which resulted as follows:

Ag present.	Cu present.	Ag found.	Diff. in per cent.	KCN in grams.	Current in OH gas.	Time in hours.	Dilution.	Remarks.
.1223	10%	.1257	+ 2.78	.5 to 1.0 gram.	1 cc. OH gas per minute.	5 to 20 hours.	200 cc.	Copper precipitated with silver.
		.1299	+ 6.20					
		.1225	+ .16					
		.1263	+ 3.20					
		.1257	+ 2.78					
		.1244	+ 1.71					
		.1251	+ 2.20					
		.1242	+ 1.55					

Later we diminished the quantity of copper, with no better result. On increasing the quantity of cyanide and also the strength of the current, the silver was very notably retarded in its deposition. After carefully repeating the work with no better outcome, we feel justified in saying that the cyanide method cannot be applied in the electrolytic separation of these two metals.

The current employed by us was obtained from storage batteries of the Julien form. Each cell contains 19 plates, each of which is 5¾ inches square. In a long experience with almost every form of battery in electrolytic work, we have not had the same even, steady current for a series of hours as we had with the Julien form, and we recommend it to all engaged in similar experiments.[1]

UNIVERSITY OF PENNSYLVANIA, *April* 13, 1889.

ON THE OCCURRENCE OF LAPACHIC ACID IN BETHABARRA WOOD.[2]

BY WM. H. GREENE AND SAMUEL C. HOOKER.

A few weeks ago we were asked by Mr. A. B. Shipley, of this city, a large importer of Bethabarra wood, to investigate the properties of a yellow substance with which the pores of the wood

[1] See further Ber. d. chem. Gesell. **21**, 2892.

[2] Read at the meeting of the Chemical Section of the Franklin Institute, April 16, 1889.

appear to be filled. So far as we know, the wood is in this country used only for the manufacture of bows and fishing-rods, for which purpose it is admirably adapted on account of its great tenacity and remarkable elasticity.

We have been able to learn nothing of the botanical nature of the tree yielding the Bethabarra wood, which is said to be brought from the West Coast of Africa, but we believe that we may venture the opinion that it is a species of Lapacho. The latter is one of the finest ornaments of the sub-tropical hills and plains of South America. Its far-spreading branches are in the spring covered with masses of flowers, red or yellow, according to the variety, so dense that the rays of the sun cannot penetrate them. Its wood is very hard, susceptible of a fine polish, and resists indefinitely the action of moisture.

The considerable cost of the wood made it desirable that some use should be found, if possible, for the refuse.

A few preliminary experiments with the extracted substance showed us that it contained a compound of much scientific interest, and for this reason we felt justified in undertaking the research, independently of any pecuniary result, with which we were not concerned.

On referring to the literature of the subject we found a paper entitled "Preliminary Notice of a New Vegetable Coloring Matter," published by Samuel P. Sadtler and William L. Rowland in December, 1880,[1] concerning the principle of the Bethabarra wood. Aside from analyses, this paper throws but little light on the constitution and properties of the substance, dealing mainly with a comparison of the color reactions of the Bethabarra principle with chrysophanic acid, santalin, haematoxylin and brasilin. The analyses of the authors left them undecided between the formulae $C_{18}H_{10}O_5$ and $C_{32}H_{32}O_4$, and they conclude their paper with a suggestion that a close relationship exists between the Bethabarra principle and chrysophanic acid and haematoxylin.

The Bethabarra wood used in our investigation was mainly in the form of sawdust. This was extracted in quantities of about five kilograms at a time, by percolation with a cold one per cent. solution of crystallised sodium carbonate; the solution was allowed to remain in contact with the wood for several hours, and then drawn off, and the operation was repeated three or four times until the intensity of the deep red color of the extract was much diminished. The liquid was then treated with an excess of hydrochloric

[1] This Journal **3**, 22.

acid, and the precipitate allowed to settle, the excess of acid being necessary to insure the rapid separation of the precipitate. The clear liquid was then siphoned off and the precipitate collected on a filter and dried.

This extract consists of the crystalline principle of the wood, accompanied by a resin, and as both are readily soluble in alcohol, this is not a desirable agent for the first crystallisation as recommended by Sadtler and Rowland. On the other hand we found the resin to be practically insoluble in ether, which freely dissolves the crystalline compound. The dry substance was powdered and shaken with ether in a closed flask; the ether was decanted off as far as possible and fresh ether added two or three times. Before decanting the last time the addition of a few drops of water is desirable, as it causes the resin to agglomerate and adhere to the walls of the flask, thus enabling the solution to be completely poured off without filtration. The ether was then distilled off, and the crystalline mass obtained was thrown on a filter and washed with a little alcohol at the pump. In this way the substance was obtained in a nearly pure condition, one recrystallisation from alcohol yielding an absolutely pure product equal in quantity to at least 0.6 per cent. of the wood employed.

After a brief examination of our substance, we were struck by the remarkable similarity of its properties with those of taiguic acid,[1] which will be found described in Gmelin's Hand-Book **16**, 521, and which has been shown by Paternò[2] to be identical with the greenhartin of Stein[3] and with the lapachic acid of Siewert.[4] Under the latter name, this substance has been the subject of an admirable research by E. Paternò,[5] who from a series of concordant analyses deduced the formula $C_{15}H_{14}O_3$, and was able to assign to it with great probability the constitution of an amylene-oxynaphthaquinone,

$$C_{10}H_4\begin{cases} CH=CH-CH(CH_3)_2 \\ O_2 \\ OH \end{cases}.$$

A close examination of the Bethabarra principle established its complete and unquestionable identity with lapachic acid. Its fusing point is 139.5°–140.5°; that of lapachic acid, as given by Paternò, is 138°.

[1] Comptes rendus **46**, 1152. [2] Gazz. chim. ital. 1879, **9**, 505. [3] J. prak. Chemie **99**, 1.
[4] La République Argentine, par R. Napp, aidé de plusieurs collaborateurs. Ouvrage écrit par ordre du Comité central Argentin pour l'Exposition de Philadelphia. Buenos Ayres, 1876.
[5] Gazz. chim. ital. **12**, 337–392.

We have prepared a number of characteristic salts. That of ammonia is unstable, losing ammonia with great readiness; a dilute solution of this salt deposits crystals of the acid when evaporated, as observed by Paternò with the ammonium compound of lapachic acid.

The silver salt is obtained as a bright red amorphous powder; on analysis we obtained the following figures:

I. 0.2594 gram gave 0.0795 gram silver.

II. 0.2674 gram gave 0.0830 gram silver.

	Found.		Calculated for $C_{15}H_{13}O_3Ag$.
	I.	II.	
Ag	30.65 per cent.	31.04 per cent.	30.95 per cent.

Mean of analyses by Paternò, 30.87 per cent. Ag. Analyses I and II were of compounds prepared separately.

By reducing agents the Bethabarra principle is converted with great facility into a white crystalline substance which rapidly absorbs oxygen from the air, being reconverted into the original compound. This also characterises lapachic acid.

By the action of concentrated sulphuric acid we have obtained a beautiful orange-red, quinone-like, crystalline substance, fusible at 155°–156° and identical with lapachone.[1] Concentrated nitric acid in the cold gives rise to the same substance, as shown by Paternò.

As the unexpectedly rapid result of our research has left us sufficient material to extend our investigations, and as the constitution assigned by Paternò to lapachone is not in accordance with some reactions which we have observed, we propose to make this compound the subject of further study.

PHILADELPHIA, *10th April*, 1889.

Communications from the Chemical Laboratory of Rutgers College.

XIX.—LECTURE EXPERIMENTS.

BY PETER T. AUSTEN.

Simple Apparatus for Showing the Formation of Nitrogen Peroxide, N_2O_4, from Nitric Oxide, N_2O_2, the Solubility of the Former in Water, the Neutrality of Nitric Oxide, N_2O_2, and the Acidity of Nitrogen Peroxide, N_2O_4.

The following simple form of apparatus has worked very satisfactorily in my lecture-room. A large cylinder, best a 1000 cc. glass-

[1] Paternò, loc. cit. 372.

stoppered graduated cylinder, is fitted with a double-bored rubber stopper, and provided with two glass-stoppered tubes. The tubes should not be over $\frac{3}{16}$ inch internal diameter, and the long one may, if desired, be drawn to a jet about $\frac{1}{8}$ inch in diameter. The cylinder is filled with water to which has been added enough litmus solution and a drop of caustic soda (not ammonia) to impart to it a deep blue color. The cylinder is next half filled with nitric oxide, N_2O_2, which must be passed through a washer filled with a 10 per cent. solution of caustic soda, in order to remove all traces of acid and the peroxide, N_2O_4, which might otherwise pass over and redden the litmus solution. The rubber stopper and tubes are introduced and pushed in tight. This is done in the deep trough in the lecture-room, care being taken that the cocks are both open, so that the tubes may be entirely filled with water. After the stopper has been inserted, the cocks are closed and the apparatus lifted out of the water. The colorless nitric oxide, N_2O_2, and the fact that it does not affect the litmus, are observed.

Holding the cylinder in a vertical position with one hand, the cock of the long tube and the cock of the short tube are successively opened with the other. Air enters through the long tube, while the water flows out through the short one. The water is allowed to flow out until the change of color of the gas is apparent. The cock of the short tube and the cock of the long tube are then successively closed, the cylinder held horizontally, and the water allowed to flow to and fro several times. The red peroxide, N_2O_4, dissolves in the water, forming nitric and nitrous acids, and the gas becomes colorless, while the blue color of the solution changes to red. The cylinder is now held vertically, and the ends of both the tubes immersed in water. A cylinder filled to the brim with water is best adapted to this, as it allows the gas-cylinder to be held well up so that it may be easily seen by all. The cock of the long tube is now opened, when the water rushes up and spurts up as a fountain, usually striking the head of the cylinder. When the vacuum has been filled by the entering water, the cylinder is

lifted up, thus removing the seal from the tubes, the cock of the short tube is opened, which allows more water to flow out and air to enter. The experiment is then repeated as just described. Four to six repetitions can usually be made before the nitric oxide, N_2O_2, is entirely consumed. The experiment is an unusually effective one.

The apparatus may be made in a simpler and cheaper form by putting in place of the glass stop-cocks on the long tube a four-inch piece of soft rubber tube, clamped at the middle by a pinch-cock, and in the short tube a Krönig valve. This form of the apparatus works in every way as well as the other, but is not so elegant.

Experiments with Gaseous Hydriodic Acid.

After some experimenting, I found the following mixture to yield hydriodic acid gas in abundant quantities: In a six-ounce flask are placed 20 grams of iodine, 5 grams of potassium iodide, 2 grams of red phosphorus, and 10 cc. of water. The whole is well mixed by swirling the flask, and then gently heated. As soon as the action begins, the flask is at once thrust under the cold-water tap until the violence of the action ceases, which occurs in a few seconds. The mixture at once ceases to evolve the gas, but on heating will evolve a large amount, the evolution ceasing as soon as the heat is removed. It is well to pass the gas through an empty Silliman washer, in order that any of the liquid which may distill over may deposit. As a rule, if the heating is too violent, no distillation will take place till toward the end. Vessels can be easily filled with the gas by displacement, the level of the gas being ascertained by introducing a lighted wax lamplighter.

Potassium chlorate placed in an iron deflagration-spoon and heated to boiling, and introduced into a jar of the gas, takes fire and burns with a large red flame, forming clouds of iodine gas and crystals. The sides of the jar become rapidly coated with a deposit of iodine crystals. The reaction is, of course, simply a flame of oxygen in hydriodic acid.

Magnesium.—I was in hope that magnesium would take the iodine away from hydriodic acid, but it does not. A piece of ribbon, when ignited and in full blaze, was dropped into the bottom of a cylinder filled with the gas. It continued to burn for an instant, and was then extinguished. There was, of course, some dissociation of the hydriodic acid.

Sodium, heated red hot and burning, was introduced into a cylinder of the gas, but behaved like magnesium.

Nitrous oxide.—The experiment is best performed by placing a cylinder of the hydriodic acid gas on a cylinder of the nitrous oxide, drawing the glass covers and allowing the gases to mix. A white cloud forms which gradually becomes reddish. Drops of red liquid collect at the bottom, and soon the tubes become filled with a cloud of minute iodine crystals, which gradually deposit on the sides. The red liquid is a solution of iodine in hydriodic acid, and soon deposits crystals of iodine. The water formed by the reaction dissolves some of the hydriodic acid, and this solution dissolves some of the iodine set free. The liquid gives off ammonia when treated with caustic alkali. The reaction appears to be $N_2O + 12HI = 2NH_4I + H_2O$.

The gradual separation and deposition of the iodine makes an interesting phenomenon. The presence of ammonia in the deposited liquid should be demonstrated.

Nitric acid gas, evolved from a mixture of granulated potassium nitrate and sulphuric acid in a small flask, and allowed to issue from a bent-up glass tip having an orifice of about one-eighth of an inch in diameter, takes fire when introduced into the gas, and burns with a fine red flame tipped with a halo of violet iodine gas and a cloud of minute iodine crystals. The sides of the vessel soon become coated with a deposit of iodine crystals.

Chlorine gas, evolving from the apparatus just described, takes fire when introduced into the hydriodic acid gas, and burns with a fine red flame resembling the preceding phenomenon. The stream of chlorine should be rapid, else no flame will be obtained, and only the separation of iodine described by Heumann will be obtained.

Sulphur dioxide makes an effective experiment, and one which is particularly appropriate in demonstrating a chemical change between gases. The cylinder full of hydriodic acid gas is placed on the one containing sulphur dioxide and the glass covers drawn. The colorless gases mix, flashing out deep red, and the sides of the cylinders are at once covered with a deposit of iodine crystals.

THE ESTIMATION OF THE TOTAL ORGANIC NITROGEN IN WATER BY THE KJELDAHL PROCESS.

By Henry Leffmann and William Beam.

Chemists will note with much satisfaction, through the recent communication of Messrs. Drown and Martin,[1] the successful application of the Kjeldahl method to the determination of the total organic nitrogen existing in waters. The so-called albuminoid ammonia process has never been more than a relative determination, and the estimation by the usual combustion method does not seem to be susceptible of general employment in this field. For the benefit of those unfamiliar with the article in question, we present the following abstract:

500 cc. of the water are poured into a round-bottomed flask of about 900 cc. capacity, and boiled until 200 cc. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask, after cooling, is added 10 cc. pure concentrated sulphuric acid. After shaking, the flask is placed in an inclined position on wire gauze, and boiled cautiously in a good drawing hood until the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a little powdered potassium permanganate added until, on shaking, the liquid acquires a green color. If the color is purple instead of green, it shows that the water has not been all driven off. After cooling, 200 cc. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 cc. of sodium hydroxide (200 grams per liter). The flask is connected with a condenser, shaken to mix the contents, and distilled. The first 50 cc. are condensed in very dilute hydrochloric acid free from ammonia. The total distillate is made up to 250 cc., mixed, and 50 cc. taken and nesslerised. A correction for the nitrogen in the chemicals used is made by means of a blank experiment. From the experiments made, Drown and Martin conclude that the nitrates and nitrites do not interfere with the accurate determination of the organic nitrogen, the error which might otherwise be caused disappearing under the conditions of great dilution which exist in natural waters.

[1] Technology Quarterly 2, 3.

Numerous observations have established the fact that the organic matter of water is susceptible of decomposition or volatilisation by simple boiling, often in such a manner that a notable proportion of the nitrogen is lost. It appeared, therefore, in experimenting on this process, that it would be advantageous to add the acid at once, and thus obtain the nitrogen existing as organic matter and also in ammonium compounds, estimating that existing in the latter in a separate sample by direct nesslerising without distillation; the calcium and magnesium which would otherwise interfere with the color reaction being removed by the addition of sodium carbonate and hydroxide, according to the suggestion of Morgan. The same principle can be extended to the determination of the ammonium formed by the sulphuric acid. Instead of distilling the liquid after rendering it alkaline, a little sodium carbonate may be added, allowed to stand, filtered, and the filter nesslerised. In this way the troublesome distillation is avoided. The procedure is as follows:

Reagents required.—Concentrated sulphuric acid as free as possible from nitrogen; that which we used was of the same make (Baker & Adamson) recommended by Drown and Martin, and contained a similar proportion of nitrogen (.05 mgm. in 10 cc.).

Sodium hydroxide free from ammonium.—100 grams of caustic soda are dissolved in about a liter of water, boiled down to about half its bulk in an open vessel, then diluted to one liter with water free from ammonium.

Sodium carbonate free from ammonium.—200 grams pure sodium carbonate are dissolved in a liter of water, and the solution boiled briskly until several hundred cc. have been evaporated.

Determination of nitrogen existing as ammonium.—200 cc. of the water are placed in a stoppered bottle, 2 cc. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of cotton in a funnel. This should be washed several times with the ammonium-free water. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 cc. of the liquid has passed through it is nesslerised. If the ammonium present is very small in quantity, a rather long and narrow tube should be used for observing the color.

Estimation of total organic and ammoniacal nitrogen.—500 cc. of the water are placed in the round-bottomed flask, 10 cc. of concentrated sulphuric acid added, and the mixture boiled down until the water is driven off and the acid is colorless or pale yellow. The potassium permanganate is then added as above, but after the green color is obtained the flask is reheated until the liquid becomes colorless; this requires but a few minutes. After cooling, 50 cc. of water are added, and then a slight excess of the sodium hydroxide solution; about 150 cc. will be required. 2 cc. of sodium carbonate solution are then added to make sure of the precipitation of the calcium and magnesium, though this is perhaps not necessary, since the caustic soda usually contains more than sufficient carbonate for this purpose. The liquid is cooled by immersing the flask in cold water, made up to 250 cc., transferred to a stoppered bottle and allowed to stand for about an hour, or until the greater portion of the precipitate has subsided. The clearer portion of the liquid is then drawn off with a pipette and run through the cotton-plug filter described above. The filtrate is perfectly clear and colorless. An aliquot portion is taken and nesslerised. We prefer to use 100 cc. and dilute to 200 cc., using rather larger glasses than are commonly employed. Drown and Martin have noted that the addition of potassium permanganate to the concentrated acid is not essential, and merely employ it as a precautionary measure. With the method detailed above, however, it will be found that unless it is used, the nesslerised liquid has a yellowish instead of brown color, and is more difficult to match. A blank experiment is to be made with the reagents used, to determine the amount of the nitrogenous impurity.

We have made trials of the method with various nitrogenous bodies of known composition, and have invariably obtained the theoretical quantity of nitrogen. As an illustration of the trustworthiness of the method the following is given: A sample represented to be pure metadiamidobenzene was purified by recrystallisation, and a solution containing one milligram—equivalent to .000259 nitrogen—added to 500 cc. water and treated as above. Only .000155 nitrogen was obtained. The experiment was repeated four times with some slight modifications of the process, but with almost precisely the same result. On examination it was found that the material used was in reality metadiamidobenzene dihydrochloride, and contained therefore .000154 nitrogen.

The following are a few of the results obtained with natural waters, and a comparison with the results by the distillation method.

PARTS PER MILLION.

Modified Process.

	Nitrogen.		
	In NH_4.	Organic.	Total.
Water, already impure, to which decomposing urine was added,	0.97	2.34	3.31
Pump-well in densely populated district, ...	0.24	0.56	0.80
Cellar water—impure, ...	0.17	0.56	0.73

Drown and Martin's Process.

	Nitrogen.			
	In Free Ammonia.	Organic.	Total.	Lost by Boiling.
Water, already impure, to which decomposing urine was added,	1.25	1.82	3.07	0.31
Pump-well in densely populated district, ...	0.33	0.38	0.71	0.09
Cellar water—impure, ...	0.23	0.41	0.64	0.09

In uncontaminated waters much less difference, and sometimes none, was noticed between the results by the original and the modified process.

The figures show conclusively, we think, even if there were no other observations on the point, that it is not safe to estimate the ammonium in the water by distillation, nor to boil the water previous to the estimation of the organic nitrogen.

715 WALNUT STREET, PHILADELPHIA.

REVIEWS AND REPORTS.

RECENT SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.

The carbohydrates constitute one of the most interesting groups of compounds in organic chemistry. In recent years these valuable and important substances have been the subject of many thorough investigations, a vast amount of knowledge concerning them has been accumulated, and the chemical characters of the individual

members of the group have become more and more clearly defined. In spite of all this, however, the attainment of the ultimate objects of chemical research, namely, the determination of their molecular constitution and their synthetical preparation, seemed, until a short time ago, as remote as ever. A very important advance has been made recently in this direction. The first steps in the synthetical preparation of the carbohydrates have been successfully taken by Emil Fischer and his co-workers of Würzburg. A synthetical sugar of the hexane series has been prepared from compounds containing a smaller number of carbon atoms. The new sugar has the composition represented by the formula $C_6H_{12}O_6$. It possesses a sweet taste and has the characteristic properties of the natural sugars, dextrose, levulose, and galactose, and like them it undergoes fermentation when mixed with yeast. It only differs from the natural sugars in being optically inactive, that is, its solution does not turn the plane of polarised light. In short, the synthetical sugar appears to bear the same relation to dextrose and levulose that racemic acid bears to dextro- and levo-tartaric acids.

Fischer's success in this field of work has no doubt been largely due to the use which he has made of phenyl-hydrazine as a means of studying the sugars. This compound was discovered by him in 1875, and is obtained by the reduction of diazo-benzene compounds. It has the power of reacting with the sugars, and indeed with all substances containing an aldehyde or ketone group. With the sugars it forms insoluble crystalline compounds, and in the case of some sugars the phenyl-hydrazine compounds are the only derivatives which can be obtained in the crystalline condition. Briefly stated, phenyl-hydrazine has become an invaluable reagent for the detection and identification of the known sugars. By means of it new sugars, prepared by synthetical processes, can be isolated and studied, and furthermore, thanks to the ingenious experiments of Fischer, sugars of one class, of which dextrose is a type, can be transformed into the isomeric class, of which levulose is a representative.

Action of Phenyl-hydrazine upon Sugars.

When phenyl-hydrazine is brought in contact with substances containing the aldehyde or ketone group, a compound called a *hydrazone* is formed. Thus with aldehyde the following reaction takes place:

$$\underset{\text{Aldehyde.}}{CH_3CHO} + \underset{\text{Phenyl-hydrazine.}}{H_2N_2C_6H_5} = H_2O + \underset{\text{Ethylidene-phenyl-hydrazone.}}{CH_3C(N_2HC_6H_5)}.$$

In a similar way, as has been shown in this Journal,[1] phenyl-hydrazine reacts with dextrose, and dextrose-phenyl-hydrazone is formed:

$$\underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Phenyl-hydrazine.}}{H_2N_2C_6H_5} = H_2O + \underset{\text{Dextrose-phenyl-hydrazone.}}{C_6H_{11}O_5(N_2HC_6H_5)}.$$

[1] This Journal **9**, 239.

Analogous hydrazones are obtained from other sugars. As a rule, they are colorless crystalline compounds, and they are precipitated in the cold by bringing together concentrated solutions of the sugar and of phenyl-hydrazine.[1] If, however, dilute solutions of the sugar and the hydrazine be heated to the temperature of the water-bath, then the reaction goes further; the hydrazone which is first formed is acted upon by more phenyl-hydrazine, and a derivative of the sugar containing two residues of the hydrazine, called an *osazone*, is formed. For example, phenyl-glucosazone is formed according to the equation:

$$\underset{\text{Glucose-phenyl-hydrazone.}}{C_6H_{12}O_5(N_2HC_6H_5)} + \underset{\text{Phenyl-hydrazine.}}{2N_2H_3C_6H_5} =$$

$$\underset{\text{Phenyl-glucosazone.}}{C_6H_{10}O_4(N_2HC_6H_5)_2} + C_6H_5NH_2 + NH_3 + H_2O.$$

Similar osazones may be obtained from other sugars. A study of their properties has shown that they are a class of stable substances. They possess a bright yellow color, and on account of their marked power of crystallisation they can be readily obtained in a state of purity. They are insoluble in water, but dissolve in boiling alcohol. As both dextrose and levulose give the same osazone when treated with phenyl-hydrazine, Fischer has given this compound the name phenyl-glucosazone. It crystallises in the form of yellow needles, which melt at 204°. It has the power of reducing Fehling's solution. So readily is this compound formed that even minute quantities of glucose can be detected by means of phenyl-hydrazine. It is only necessary to mix the solution supposed to contain the sugar with an acetic acid solution of phenyl-hydrazine and to heat on the water-bath; if sugar is present, a bright yellow crystalline precipitate will be formed.[2] In a similar manner other osazones are prepared from other sugars, and, owing to their insolubility and great crystallising power, they have become a valuable means of detecting and identifying the sugars. The following is a table of the melting points of the osazones which have thus far been prepared:

Glucosazone,	$C_{18}H_{22}N_4O_4$,	m. p. 204°	from	dextrose. / levulose.
Galactosazone,	"	" 193°	"	galactose.
Sorbosazone,	"	" 164°	"	sorbose.
Xylosazone,	"	" 160°	"	xylose.
a-Acrosazone,	"	" 204°	"	*a*-acrose.
β- "	"	" 148°	"	*β*- "
Rhamnosazone,	$C_{18}H_{22}N_4O_3$	" 180°	"	isodulcite.
Arabinosazone,	$C_{17}H_{20}N_4O_3$	" 158°	"	arabinose.
Erythrosazone,	$C_{16}H_{18}N_4O_2$	" 167°	"	erythrose.
Lactosazone,	$C_{24}H_{32}N_4O_9$	" 200°	"	milk sugar.
Maltosazone,	$C_{24}H_{30}N_4O_8$	" 191°	"	maltose.
Glycerosazone,	$C_{15}H_{16}N_4O$	" 131°	"	glycerose.

[1] Ber. d. chem. Ges. **20**, 824.

[2] Ber. d. chem. Ges. **22**, 90. Best method of conducting the test.

Cane sugar is inverted by the action of phenyl-hydrazine, and glucosazone, m. p. 204°, is obtained.

A study of the action of phenyl-hydrazine upon other substances heretofore classed with the glucose group has shown that some of these substances belong to other classes of compounds. Thus inosite, dambose, and scyllite, although they possess the same formula as the glucoses, do not react with phenyl-hydrazine, nor do they reduce Fehling's solution, consequently they are no true carbohydrates. Kiliani[1] has shown that arabinose has the formula $C_5H_{10}O_5$; this fact has been confirmed by a study of the behavior of the compound with phenyl-hydrazine.[2] Mannitose[3] was found to be identical with levulose, while phlorose[4] was identical with dextrose; crocose,[5] on the other hand, was found to consist of a mixture of dextrose with another sugar, the nature of which has not yet been determined. Quercite is an aromatic compound, while isodulcite,[6] $C_6H_{14}O_6$, hitherto regarded as a hexacid alcohol, isomeric with dulcite and mannite, was found to be a sugar belonging to the arabinose group.

In regard to the constitution of the hydrazones and the osazones of the sugars, it seems very probable, from all that is known in regard to these compounds, that in the hydrazones the group $-C=N_2HC_6H_5$ is present, while the group characteristic of the osazones is $-C=N_2HC_6H_5$ / $-C=N_2HC_6H_5$. If then Kiliani's[7] formulas for dextrose and levulose be accepted, the formula for dextrose-phenyl-hydrazone[8] would be

$$HC-(CHOH)_4-CH_2OH$$
$$\|$$
$$N_2HC_6H_5$$

and for glucosazone,[9]

$$CH\text{——}C-CHOH-CHOH-CHOH-CH_2OH$$
$$\|\qquad\|$$
$$C_6H_5N_2H\quad N_2HC_6H_5$$

The compounds derived from other sugars would be similarly constituted. It was also observed that the hydrazine derivatives of the natural sugars are optically active, that is, have the power of turning the plane of polarised light.

Transformation of the Osazones into Sugars.—It is then an easy matter, by the methods described, to change a sugar into its corresponding hydrazone or osazone, and these compounds, as has been pointed out above, are one of the best means of detecting and identifying the known sugars, as well as of isolating new mem-

[1] Ber. d. chem. Ges. **20**, 339. [2] Ibid. **20**, 825. [3] Ibid. **20**, 826. [4] Ibid. **21**, 988.
[5] Ibid. **21**, 988. [6] Ibid. **21**, 2173. [7] Ibid. **18**, 3066; **19**, 221, 767, 1910. [8] Ibid. **20**, 821.

bers of the series. A method of bringing about the reverse change, that is, of transforming a hydrazone or an osazone into sugar, is also very desirable. For if by synthetical processes a new sugar should be made which could be detected by the phenyl-hydrazine reaction, then the problem would still remain of converting the osazone into the sugar itself. This problem, which proved to be a most difficult one, has also been successfully solved by Fischer.

The following method was used for decomposing the hydrazones.[1] Treated with cold concentrated hydrochloric acid they are dissolved, and on warming, crystals of phenyl-hydrazine hydrochlorate separate, and the sugar remains in the solution. The decomposition of the hydrazones was effected in still another way.[2] When treated with zinc dust and acetic acid they are converted into amines and aniline, according to the general equation:[3]

$$\begin{array}{l} | \\ C{=}N_2HC_6H_5 \\ | \end{array} + 4H = \begin{array}{l} | \\ HC{-}NH_2 \\ | \end{array} + C_6H_5NH_2.$$

Hydrazone. Amine. Aniline.

The amines are then converted into the corresponding hydroxyl derivatives by the action of nitrous acid.

The transformation of osazones into sugars did not take place so readily as in the case of the hydrazones. The first method employed by Fischer was the same in principle as that which has just been described, namely, reduction with nascent hydrogen, and treatment of the base which is thus formed with nitrous acid. Thus, when phenyl-glucosazone was reduced, a base having the formula $C_6H_{13}NO_5$,[4] and called isoglucosamine, was obtained, and further treatment of this base with nitrous acid converted it into levulose.

It is possible, therefore, to transform dextrose into levulose. The former sugar, by the action of phenyl hydrazine, is converted into glucosazone; the glucosazone, by reduction, yields isoglucosamine, and the latter compound, under the influence of nitrous acid, is transformed into levulose.

The yield of sugar by this method was far from being a satisfactory one, and much better results were obtained in the following way: The osazone was dissolved in cold fuming hydrochloric acid. A dark red-colored solution was formed, which, after standing for some time, gave a deposit of crystals of phenyl-hydrazine hydrochlorate, and from the solution a compound was obtained which differed from the osazone in having, in place of

the group $\begin{array}{l} | \\ C{=}N_2HC_6H_5 \\ | \\ C{=}N_2HC_6H_5 \\ | \end{array}$ of the osazone, the double ketone

[1] Ber. d. chem. Ges. **20**, 824. [2] Ibid. **20**, 825. [3] Ibid. **19**, 1925. [4] Ibid. **19**, 1920.

group[1] $\begin{matrix} | \\ C=O \\ | \\ C=O \\ | \end{matrix}$. As the method was found to be a general one and applicable to all osazone, the new class of compounds thus obtained were called *osones.* Thus from glucosazone, having the formula $\begin{matrix} HC- & C-(CHOH)_3-CH_2OH, \\ \| & \| \\ C_6H_5N_2H & HN_2C_6H_5 \end{matrix}$ the compound $\begin{matrix} HC-C-(CHOH)_3-CH_2OH \\ \| \quad \| \\ O \quad O \end{matrix}$, called *glucosone,*[2] was obtained. It has also been called oxyglucose, because it may be regarded as an oxidation product of both dextrose and levulose. When treated with nascent hydrogen the osones are converted into sugars.[3] Glucosone, when reduced with zinc dust and acetic acid, was converted into levulose. A much larger yield of sugar was obtained by this method than by the one first described, and it has been successfully employed in converting other osazones into sugars. The following sugars have been prepared from osazones:[4]

Levulose	from	Glucosazone,
Galactose	"	Galactosazone,
Sorbose	"	Sorbosazone,
Lactose	"	Lactosazone,
Maltose	"	Maltosazone,
Arabinose	"	Arabinosazone,
Isodulcite	"	Rhamnosazone,
α-Acrose	"	α-Acrosazone.

In all these cases the transformation took place quite readily. More difficulty was experienced in the case of osazones containing less oxygen, as, for example, erythrosazone and glycerosazone.

As each osazone, by the action of hydrochloric acid, is converted into an osone, and as the latter compounds are closely related to the sugars, it is interesting to note that they readily react with phenyl-hydrazine, and the original osazone is regenerated. Thus glucosone, like dextrose and levulose, with phenyl-hydrazine gives glucosazone. Like these sugars, it also has the power of uniting with hydrocyanic acid, and, by appropriate treatment, levulinic acid and furfurol may be obtained from it. As the reduction of glucosone converts it into levulose, another method of passing from dextrose to levulose, better than the one first discovered, is to convert the dextrose into glucosazone, to treat this with concentrated hydrochloric acid and thus obtain glucosone, and then to reduce the latter compound with nascent hydrogen. In

[1] Ber. d. chem. Ges. **21**, 2631. [2] Ibid. **22**, 87. [3] Ibid. **22**, 94. [4] Ibid. **22**, 89.

fact, the method is a general one for changing all natural sugars containing the aldehyde group into the isomeric sugars having the ketone group.

Synthetical Experiments.—As the sugars may be regarded as aldehyde and ketone alcohols obtained by the partial oxidation of the hexacid alcohols, it was natural to apply the phenyl-hydrazine reaction to the oxidation products of other poly-acid alcohols, to determine whether compounds analogous to the sugars are not formed when these substances are oxidised. It had long been known that when glycerin is oxidised, a liquid possessing the power of reducing Fehling's solution is obtained. By oxidising glycerin with nitric acid and treating the oxidation product with phenyl-hydrazine, Fischer[1] obtained a beautiful crystalline osazone, which was found to have the formula $CH_2OH - CN_2HC_6H_5 - HCN_2HC_6H_5$, and which had undoubtedly been formed from glycerin aldehyde, or the isomeric compound, dioxyacetone. In a similar manner the compound $C_4H_6O_2(N_2HC_6H_5)_2$ was obtained from the oxidation products of erythrite, while from dulcite a compound isomeric with glucosazone was obtained. A study of these derivatives showed that they belong to the class of osazones, and they were named accordingly. Thus the one obtained from glycerin was called glycerosazone, while the one from erythrite was called erythrosazone; the former melts at 131°, the latter at 167°. Mannite[2] was also oxidised with nitric acid, and among the oxidation products, besides levulose, a new sugar, called *mannose*, was discovered. A careful study of mannose has shown that it has the same constitution as dextrose, and that the isomerism can only be explained by the Van't Hoff and Le Bel hypothesis.

The preliminary experiments on the oxidation of glycerin indicated that the immediate oxidation product, glycerose, consists either of glycerin aldehyde or dioxyacetone, or of a mixture of both. The attempt was next made to prepare glycerin aldehyde from bibrom-acrolein. The latter substance was treated with dilute baryta water, and a soluble compound, having strong reducing properties and resembling the aldehyde alcohols, was obtained. Many attempts were made to isolate this substance, because it was hoped by means of it to effect the synthesis of a sugar; but it was only by means of the phenyl-hydrazine reaction that trustworthy results were obtained. From the decomposition products of bibrom-acrolein an osazone of the hexane series, having the formula $C_{18}H_{22}N_4O_4$,[3] was obtained. This synthetical compound, called "acrosazone," to indicate that it had been formed from acrolein, showed the greatest resemblance in properties to glucosazone. It melts at the same temperature, namely, 205°, and in appearance can scarcely be distinguished from it. At the same time a small quantity of an osazone, isomeric with the

[1] Ber. d. chem. Ges. **20**, 1088. [2] Ibid. **21**, 1805, and **22**, 365. [3] Ibid. **20**, 1088.

one just described and melting at a lower temperature, was found. To distinguish between the two, the former was called *α*-acrosazone, the latter *β*-acrosazone. The striking similarity in properties of *α*-acrosazone and glucosazone indicated that the former was derived from a compound having the formula $C_6H_{12}O_6$, and that this carbohydrate must have been formed from the acrolein bromide by some such reaction as the following one:

$$2C_3H_4Br_2O + 2BaO_2H_2 = C_6H_{12}O_6 + 2BaBr_2.$$

To obtain the new compound, which appeared to be a sugar, from *α*-acrosazone, the latter substance was reduced with nascent hydrogen, and the amine thus formed was treated with nitrous acid. A substance possessing all of the ordinary properties of the sugars was obtained. The yield was so small, however, that not sufficient of the compound was obtained for a more detailed study of its properties.

To obtain larger quantities of the *α*-acrosazone, and so of the synthetical sugar, glycerin was oxidised with bromine in alkaline solution.[1] The oxidation product, called glycerose, was mixed with dilute alkali and allowed to stand four or five days. The object of this procedure is to bring about a condensation of the compounds contained in the glycerose. Phenyl-hydrazine was thereupon added to the liquid, and a precipitate consisting of *α*- and *β*-acrosazone was formed. The *α*-acrosazone was readily separated from the *β*-compound by means of acetic ether. For the purpose of obtaining the new sugar from *α*-acrosazone, the second method mentioned above, and which by this time, in the course of the investigations, had been found to give good results in the conversion of glucosazone into levulose, was employed. Concentrated hydrochloric acid transformed the *α*-acrosazone into a compound almost identical with glucosone in properties. This substance, called *α*-acrosone, like glucosone, combines with ortho-toluylenediamine and forms a crystalline compound, and when boiled with hydrochloric acid it yields levulinic acid. It reacts with phenyl-hydrazine, and the original *α*-acrosazone is regenerated. Heated with water in a sealed tube to a high temperature, furfurol is formed. Glucosone when reduced is converted into levulose, so the *α*-acrosone when treated with zinc dust and acetic acid is converted into a compound $C_6H_{12}O_6$, called *acrose*, which in all of its properties shows the closest similarity to the natural sugars. It has a sweet taste and reduces Fehling's solution. Its solution when mixed with an acetic acid solution of phenyl-hydrazine gives, at the temperature of the water-bath, an abundant precipitate of *α*-acrosazone. The aqueous solution of acrose can be readily fermented by means of yeast. Reduction of dextrose and levulose with sodium amalgam converts them into mannite, $C_6H_{14}O_6$. So also reduction of the acrose by the same means gave a compound $C_6H_{14}O_6$ called *acrite*, which in properties showed the greatest resemblance to mannite. The only difference

[1] Ber. d. chem. Ges. **20**, 3384.

between the acrose, acrosone, acrosazone and acrite, on the one hand, and the corresponding derivatives of dextrose or levulose, on the other, is that while the latter are optically active and rotate the plane of polarised light, the former are optically inactive. That Fischer will succeed in converting acrose into an optically active sugar by zymogenic fermentation seems highly probable.

The synthetical sugar acrose is unquestionably a member of the glucose group. As it is formed by the polymerisation of the oxidation products of glycerin, experiments were undertaken for the purpose of determining the nature of glycerose, as these oxidation products are called. It was found that almost pure glycerose could be obtained by the action of bromine vapor upon lead glycerate.[1] It was suspected that the glycerose consisted either of glycerin aldehyde or of dioxyacetone, or of a mixture of both these compounds. That the latter view was the correct one was shown by treating the glycerose with hydrocyanic acid[2] according to Kiliani's method, and saponifying the resulting compounds. Oxyacids were thus formed. One of these, which was present in small quantity, seemed to be identical with erythroglucinic acid; the other, which was the chief product of the reaction, was proved to be the heretofore undiscovered trioxybutyric acid. As the trioxybutyric acid could only have been formed from dioxyacetone, it appears from these experiments that the latter substance is the chief constituent of glycerose, but at the same time there seems to be some of the isomeric glycerin aldehyde present.

Acrose has been obtained by still another method. It was observed by Butterow,[3] afterwards by Tollens,[4] and more recently by Loew,[5] that when formic aldehyde is treated with lime water, a polymerisation product is obtained which has the power of reducing Fehling's solution. Loew has given the substance the name "formose," and he regarded it as a member of the glucose series of sugars. Fischer[6] has recently shown that it is a mixture of several aldehyde or ketone alcohols which can be separated by means of phenyl-hydrazine. He succeeded in isolating *a*-acrosazone, thus proving that one of the compounds formed by the polymerisation of formic aldehyde is a sugar of the glucose series. This fact is all the more interesting when it is remembered that acrose is closely related to the natural sugars, dextrose and levulose—in fact, appears to be the "inactive" modification of these compounds. At all events, these experiments make Baeyer's theory of plant assimilation appear more probable. According to this theory, glucose is formed in plants by the polymerisation of formic aldehyde, the latter substance being produced in the leaves by the reduction of carbonic acid.

E. H. KEISER.

[1] Ber. d. chem. Ges. **21**, 2634. [2] Ibid. **22**, 106. [3] Ann. der Chem. (Liebig) **120**, 295.
[4] Ber. d. chem. Ges. **15**, 1629. [5] J. prakt. Chem. (2), **33**, 321; **34**, 51.
[6] Ber. d. chem. Ges. **22**, 359.

NOTES.

A Vexatious Mixture for Qualitative Analysis.[1]

In most of the methods of qualitative analysis, silver is detected in the hydrochloric acid group, and if not detected there, is not sought for further. There are cases, however, in which such a procedure may lead to a failure to detect silver, when the method is carried out by students. The following mixture proves, as a rule, very vexatious to beginners, and even men of experience have fallen under its baneful influence, when asked to test the solution for silver alone.

Concentrated hydrochloric acid is added to a ten per cent. solution of silver nitrate until the silver is all precipitated as chloride and some excess of hydrochloric acid is present. The liquid is then neutralised with strong ammonia, and some excess over the amount required to dissolve the silver chloride is added. Hydrochloric acid is again added until the liquid is acid. The solution now contains the double chloride of silver and ammonia (Faraday), and is not precipitated by hydrochloric acid. It is precipitated by water, however, and the precipitate so formed is redissolved on the addition of hydrochloric acid.

To the solution[2] are now added solutions of tartar emetic, bismuthic nitrate in dilute nitric acid, and cupric nitrate, the resulting turbidity being cleared up after each addition with a little hydrochloric acid. The mixture is then given out for analysis. The student begins by diluting the liquid and gets a white precipitate, which redissolves in an excess of hydrochloric acid to a clear liquid. He ascribes this to the presence of bismuth or antimony, and notes the absence of the hydrochloric acid group. He finds in their proper places antimony, bismuth and copper. He is quite sure that silver is not present, as the absence of a precipitate by hydrochloric acid excludes it. When he finds later on that the original acid solution contains hydrochloric acid in large amounts, since it yields a heavy precipitate with silver nitrate, he is doubly certain, nor can he be blamed for his false inference.

The bismuth is removed with ammonia, and the filtrate precipitated with hydrogen sulphide. The resulting precipitate of copper sulphide and silver sulphide is boiled with dilute sulphuric acid, filtered, and tested for cadmium. None is found. Copper has announced its presence by the blue color with ammonia in

[1] Communication from the Chemical Laboratory of Rutgers College.

[2] This is, of course, but an example of many mixtures that can be made, any of which will make trouble with the mechanical or routine analyst.

making the bismuth test. There is hence no need to examine the precipitate of copper sulphide and silver sulphide. The silver has escaped detection.

If the amount of silver present as double chloride of silver and ammonium is small, and a considerable amount of mercuric chloride is present, and the sulphides are not well washed out, a considerable amount of ammonium chloride will stay in the precipitate. When this precipitate is dissolved in nitric acid, *aqua regia* will be formed, and will convert the silver into the chloride, which, being practically insoluble, will remain with the mercuric sulphide residue, and will hence escape detection altogether, or it will be called lead sulphate, if lead is also present.

The remedy for the first oversight is to test the nitric acid solution of the group sulphides of the fifth group with hydrochloric acid before testing for lead with sulphuric acid. If desired, any lead which goes down as the chloride with the silver chloride, may be separated with hot water. Such a procedure is laid down in some of the small German text-books. The point should not be overlooked, and should be demonstrated in the lecture course; for even an experienced chemist may easily make a mistake in such an unexpected case as this.

The remedy for the second oversight is not as simple as it may appear. To get the student to make satisfactory separations in qualitative analysis is not an easy task. In fact, it is rarely accomplished until after he has had some experience in quantitative work. I believe that better results in the teaching of qualitative analysis would be obtained if the course in analytical chemistry were to begin with a certain number of quantitative analyses of pure substances. Following them should come the study of qualitative analysis; and following this, again, the remainder of the course in quantitative analysis. This is essentially the plan advocated by Dr. Muck of Bochum.

PETER T. AUSTEN.

New Researches proving that the Poisonous Effect of Exhaled Air is not due to Carbon Dioxide.

In a previous paper by Brown-Sequard and d'Arsouval, the relation between exhaled air and certain forms of disease was investigated. In these researches the same writers show that this air contains a poison (either simple or complex) which can produce death even when not directly injected into the blood. The effect of breathing this air was investigated by means of an apparatus, the essential parts of which are as follows:

A series of air-tight metallic cases were connected with one another, and a current of air drawn through the series by means of a suction pump. Into each of these cases was placed a rabbit. The rabbit in the first case thus breathed only pure air; those in the succeeding cases breathed the air which came from the pre-

ceding cases, which was therefore more and more contaminated. Young rabbits (from 5 to 7 weeks old) died very quickly, with the exception of those in the first and the second cases. Those in the last two cases sometimes died in 2 or 3 days. If a dying rabbit were removed and placed in pure air, it recovered after 5 to 10 days. With large rabbits the general results were the same, and only differed in regard to the time. There was never more than six per cent. of carbon dioxide in the last of the cases, but it was deemed advisable to prove that this did not cause the death of the rabbits. The air could not be passed through caustic alkali in order to remove the carbon dioxide, for the alkali also destroyed or absorbed the poison. By passing the air through a tube filled with glass beads moistened with strong sulphuric acid, the poisonous matter was destroyed and the carbon dioxide left unchanged. By placing such a tube between the sixth and seventh cases, it was found that the rabbit in the seventh case did not die, thus proving that carbon dioxide was not the cause of the death of the rabbits. In a number of other experiments the authors have shown that air containing a considerable percentage of carbon dioxide (free from hydrochloric acid) can be breathed with impunity by men, rabbits, dogs, etc. They themselves remained for several hours in an atmosphere containing 20 per cent. of carbon dioxide without experiencing the slightest inconvenience.

If the poison contained in exhaled air be absorbed, and the solution injected into an animal, death generally results. The solution may be heated to 100° C. without destroying its properties in this respect, thus showing that its effects are not due to microbes.—(*Comptes rendus*, 1889, **108**, 267).

RUDOLF DE ROODE.

On the Valence of Aluminium.

The subject of the molecular weight of aluminium has again been under investigation, this time by A. Combes. The substance used was the acetyl-acetonate of aluminium, $[Al(C_5H_7O_2)_3]_x$. This was obtained in a very pure condition as a white solid, melting at 193°–194°, and boiling without decomposition at 314°–315° (cor.).

The vapor density was determined by V. Meyer's method, in an atmosphere of pure, dry nitrogen at the temperature of boiling mercury. Two consecutive determinations gave the following figures:

Weight of substance.	Volume of gas.	Temperature.	Barometer.	Tension of aqueous vapor.
0.2105 gram.	15.2 cc.	14.5°	771.5 mm.	12.3 mm.
0.1798	13.1	15	770.9	12.7

Density.		Molecular Weight.	
Found.	Calculated.	Found.	Calculated for $Al(C_5H_7O_2)_3$.
11.27 }	11.236	325.5 }	324.5
11.23 }		324.2 }	

The volatilisation took place in a very regular manner and without decomposition. After cooling, the substance appeared in perfectly colorless crystals, completely soluble in alcohol. The results of these experiments show, therefore, that the acetyl-acetonate of aluminium is not altered at a temperature of 360° in an atmosphere of nitrogen, and that its vapor density at this temperature (only 45° above its boiling point) corresponds to the formula $Al(C_5H_7O_2)_3$, and not $Al_2(C_5H_7O_2)_6$.—(*Comptes rendus*, 1889, **405**.)

RUDOLF DE ROODE.

The Life of Avogadro.

The following facts of interest concerning the life of Avogadro, about which very little is generally known, are taken from a notice in the *Chemiker-Zeitung* **13**, 17, by Professor Hugo Schiff, of Florence:

Amedeo Count Avogadro, son of the magistrate Filippo Vercellone, was born in Turin, August 9, 1776. He studied jurisprudence at the Turin University, became Doctor of Laws on March 16, 1796, and then held a position under the government until 1806, at which time he began his career as a scientist. In physics he was self-taught, and obtained a subordinate position in the Collegio delle Provincie in Turin, which was then, and still is, a richly endowed department of the Turin University. On Nov. 7, 1809, he became Professor of Physics at the Gymnasium in Vercelli. In 1820 he was elected Professor of Mathematical Physics at the Turin University. Later this chair of instruction was abolished, and Avogadro resumed the practice of law. He was, however, reinstated in his chair through the influence of Charles Albert, and remained at the university until 1850, when he retired on account of old age and ill health. He died in Turin, July 9, 1856, at the age of 80 years.

Avogadro was but little known in Italy and unknown in foreign countries. He shared with Charles Gerhard, who died in the same year, Aug. 19, 1856, the same fate. It was only after death that their great and important contributions to science found recognition.

RUDOLF DE ROODE.

Michel Eugene Chevreul.

This distinguished chemist, whose name has been and will be so familiar to scientists on account of his classic researches on the fats and also on various dye-stuffs—to the world in general on account of his marvellous longevity—has at last shared the common fate of all. He died in Paris, April 9, 1889, at the age of 102 years. Born in Angers on Aug. 31, 1786, he went to Paris in 1803, and in 1806 was appointed Director of Vauquelin's Laboratory and Professor in the Lycée Charlemagne. He also occupied other positions of importance and honor. He was a member

of the Academy of Sciences, and never failed to attend its meetings up to his one hundredth birthday, on which occasion he was the recipient of much distinction and honor. Chevreul was a careful observer and faithful student of nature, his work being characterised by its accuracy and thoroughness. The larger part of his researches was upon fats and oils. The principal journals of the day from 1806 to 1876 contained numerous articles from his pen. In 1823, the work on fats and oils which had from time to time appeared in the current journals was arranged in systematic order, and published under the title "Recherches sur les corps gras." It formed a volume rich in valuable information. Few fields of chemistry had been so thoroughly worked out, and these researches formed a great contribution both to science and the arts. Considering the very small advance which had been made in the field of organic chemistry, this work of Chevreul, as well as almost everything which he undertook, showed him to be a man far in advance of his time. Next in importance to his researches upon the fats were those upon various dye-stuffs, the results of which were communicated to the Academy of Sciences of Paris, under the title "Recherches sur la teinture." In this communication he reviewed exhaustively the dye-stuff industry of the day; proposed a theory of complementary and of mixed colors; and again presented to science and art a great contribution. His other researches were of minor importance, yet worthy of careful attention and study. Notwithstanding his great age, Chevreul retained his deep interest in science and kept up with the times to the last.

R. DE R.